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**FORMATION OF STRUCTURE AND PROPERTIES  
BY HEAT TREATMENT IN HIGH-STRENGTH  
Fe-Ni-C INVAR ALLOYS, DOPED WITH COBALT,  
VANADIUM AND MOLYBDENUM**

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# ABSTRACT

**In the introduction** substantiate the actuality of the topic of the dissertation, formulated purpose and objectives of the study, are shown scientific novelty, the practical significance of the work, reflects the main provisions for the defense, confidence and personal contribution of the author.

**In the first chapter** reviewed domestic and foreign literature sources, discusses the physical causes of low coefficient of linear expansion of Invar alloys. Examples of various chemical compositions of Invar alloys are given and their use is considered. Analyzed the shortcomings of classical Invars and defined prerequisites for improving the mechanical properties of them.

Considered the effect of chemical composition on the structure, mechanical and special properties of Invar alloys. It is shown that without the heat treatment is not possible to obtain simultaneously low values of coefficient of linear expansion and increased strength properties. Analysis of literature sources shows that there are only a few scattered data on the effect of heat treatment on mechanical properties of high strength Invar alloys with a low coefficient of linear expansion. There is no consensus about the effect of temperature and time of heat treatment parameters. Formulated the purpose of the work and supplied the research problem.

**The second chapter** describes the materials and experimental techniques. To investigate were selected Invar alloys based on Fe-Ni system, alloyed with carbon and carbide forming elements, which from the literature should ensure the hardening of these alloys due to the dispersed carbide phase. Doping cobalt is used to reduce the coefficient of expansion.

The alloys were melted in a vacuum induction furnace at 60 kg ingots, forged and then rolled into rods. Heat treatment of the samples was carried out in a

laboratory electric furnace PL-20 with thermo-control unit and made the following modes:

- Quenching from temperature 1200 and 1250 °C with cooled in water and oil;
- Heating the quenched samples at temperatures of 300, 500, 600, 650, 700 and 800 °C, soaking for 1 hour and air cooling;
- Heating the samples at 80 °C and soaking for 48 hours.

The microstructure was investigated under an optical microscope Meiji Techno and scanning electron microscope JEOL JSM-6490LV with microprobe analysis system INCA Energy 450. The quantitative analysis was performed using Thixomet PRO – computer image analysis system. The amount of the statistical sample consisted of 150 to 300 units. Relative measurement error does not exceed 5-7%.

X-ray diffraction (XRD) was performed on diffractometer SHIMADZU XRD-7000 with X-ray chrome anode tube ( $\lambda = 2.285 \text{ \AA}$ ) at a voltage of 40 kV and a current of 30 mA. Determination of the phase composition was carried out in a software package International Centre for Diffraction Data PDF-2 Release 2014 with an integrated database in it.

The hardness was measured by Vickers in accordance with GOST 2999-75 on the universal hardness tester Test M4S075G3 Emso diamond pyramid indentation under a load of 29.42 N (3 kgf) and the exposure time under a load of 15 seconds. The strength characteristics of the material was determined according to GOST 1497-84 in a tensile test specimens with cylindrical working portion 30 mm long and 6 mm on a universal testing machine AG-IC 300 kN SHIMADZU.

Modelling of heat treatment and the determination of coefficient of linear expansion was performed on samples 10 mm diameter and 80-90 mm length on Gleeble 3500 complex, that keeps homogenous temperature in the cross-sections center of the sample at different heating or cooling modes with

different speeds. For dilatometric tests using high-precision sensor, whose resolution is 0.4 micron. Thermal testing regime to determine the coefficient of linear expansion corresponded to GOST 14080-78.

**The third chapter** presents the results of studies of alloys structure before and after hardening.

The hot rolled rod structure consists of grains of metal base and second-phase particles of different sizes. Analysis of the microprobe results showed that the spectra of the metal base in all alloys are found peaks iron, nickel, carbon, and cobalt - in 32NKF alloy, molybdenum - in 34NFM alloy, and vanadium - in alloys 32NF, 32NFK, 34NFM. XRD analysis allowed to identify the matrix alloy as the  $\gamma$ -solid solution with FCC lattice containing these elements.

Distribution map of chemical elements and micro-roentgen spectra recorded from certain inclusions demonstrate that they are concentrated carbon, vanadium, molybdenum, titanium, and almost no detectable iron, nickel and cobalt, which allowed identify these particles as carbides of the alloying elements.

In the structure also observed large particles, in which by microprobe analysis indicates the presence of a number elements typical for nonmetallic inclusions metallurgical origin. These particles preferably have a rounded shape, which confirms their separation from the melt. The chemical composition and quantity of non-metallic inclusions when used for smelting alloys with five variants deoxidizing compositions were different. Based on the results of microscopic analysis, electron microscopy and electron microprobe analysis, it was found that the most suitable deoxidizer composition is: 0.15%  $Mn_{raf}$ , 0.35% NiMg (0.15% Mg), 0.1%  $Si_{cr}$ , 0.1 % SiCa, 0.06% Al and 0.07-0.1%  $Ti_{sponge}$  that provides a smaller number, smaller size, and the most favorable form of non-metallic inclusions of metallurgical origin.



After quenching from 1200 and 1250 °C in water and in oil in structure fixed metal base grain and carbide particles with different sizes, besides cooling medium does not have any significant effect on the character of the structure. Explanation diffraction patterns obtained by XRD, showed that all the metal base of the alloys, as well as in the initial hot rolled condition has FCC lattice, i.e. polymorphic  $\gamma \rightarrow \alpha$  transformation during quenching is absent. By increasing the heating temperature for quenching is observed increase in grain size and reducing the number of the carbide particles in comparison with the initial state, as confirmed by quantitative analysis.

Dilatometric method of analysis determined that dissolution of the carbide phase during heating for quenching begins at a temperature of 950-960 °C and continues for isothermal holding, as evidenced by the characteristic inflections in the dilatometric curves of the alloys.

X-ray studies have shown that the diffraction patterns of quenched samples of all three of the alloys, observed a shift characteristic peaks reflections from crystallographic planes compared with the initial state. Was found lattice parameters change of  $\gamma$ -solid solution on the basis of the calculated results of XRD, which indicates a change in alloying  $\gamma$ -solid solution during hardening due to the transition to it and the carbon atoms of the alloying elements of the carbide phase, dissolved under heating.

**The fourth chapter** presents the results of studies of the structure and mechanical properties of Invar alloys subjected heating after quenching. An increase in temperature from 300 to 650-700 °C is accompanied by an increase in hardness, and at higher temperatures up to 800 °C causes its decline.

The hardness and tensile strength after heating samples previously quenched from a high temperature 1250 °C, was greater compared to the properties of samples quenched from a lower temperature of 1200 °C. In this case the cooling medium has no significant effect on the hardness of the samples after the heat,

so heat treatment as a quenching medium water can be recommended as a more eco-friendly.

The maximum hardening is provided by precipitation hardening with release of resistant carbides of alloying elements during thermal treatment, which consists in quenching from 1250 °C in water, followed by aging at 700 °C for 1 h and stabilization at 80 °C for 48 h. It provides: for 32NF alloy hardness is 400 HV, UTS = 1150 H/mm<sup>2</sup>,  $\sigma_{0.2}$  = 1030 H/mm<sup>2</sup>,  $\alpha$  =  $1.3 \times 10^{-6}$  K<sup>-1</sup>, for 34NFM alloy hardness is 300 HV, UTS = 870 H/mm<sup>2</sup>,  $\sigma_{0.2}$  = 780 H/mm<sup>2</sup>,  $\alpha$  =  $2.4 \times 10^{-6}$  K<sup>-1</sup>. 32NFK cobalt alloy for the heat treatment regime is quenched from 1250 °C in water, followed by aging at 650 °C and stabilizing at 80 °C for 48 hours and it provides hardness 250 HV, UTS = 800 H/mm<sup>2</sup>,  $\sigma_{0.2}$  = 720 H/mm<sup>2</sup>,  $\alpha$  =  $1.67 \times 10^{-6}$  K<sup>-1</sup>.

After heating, the large particles are observed in the base metal alloys which are not fully dissolved during heating for quenching, and the dispersed particles size of from 70 to 320 nm. Quantitative analysis showed that the relative proportion of coarse particles after the heating quenched sample has not changed in comparison with the hardened state, and the number of particulate by increasing the heating temperature from 300 to 700 °C increased. This demonstrates the isolation this particles during decomposition of saturated solid solution obtained by quenching. Using the method of microanalysis particles were identified as carbides containing vanadium. The formation of intermetallic phases characteristic of system Fe-Ni, was not found and confirmed by the results of XRD and carbides formula can be described as VC (V<sub>4</sub>C<sub>3</sub>).

When interpreting diffraction patterns obtained by X-ray diffraction revealed that after aging the quenched alloy samples, observed the shift characteristic reflection peaks. The calculated lattice parameter as compared to the hardened state of change, that indicates a change in alloying of  $\gamma$ -solid solution during

aging, as a result of the transition of carbon atoms and carbide-forming elements in the precipitate carbide phase. Dilatometric method of analysis characteristic changes in the angle of the curves were recorded, which is also evidenced by the allocation of dispersed carbide particles during aging.

The higher heating temperature for quenching provide more complete dissolution of initial carbide particles greater saturation of the solid solution carbon and alloying elements, and, as a result, a greater effect precipitation hardening in its decay, which explains the higher hardness. Reduction of hardness with increasing aging temperature to 800 °C coagulation is explained carbide particles, as shown by microstructural studies.

In the alloy 34NFM molybdenum is present mainly in large carbides, which do not completely dissolve when heated for hardening,  $\gamma$ -solid solution slightly saturated with molybdenum, and the proportion of dispersed molybdenum carbides released during subsequent heating, insignificant. Therefore, doping of molybdenum in reducing the content of carbon and vanadium in the alloy 34NFM was less effective for precipitation hardening as compared with the alloy 32NF doped vanadium only: the maximum hardness of the alloy during aging 34NFM was 100 HV, and the tensile strength - 450 N/mm<sup>2</sup> below, than 32NF alloy.

The alloy 32NFK observed least amount dispersed carbide particles precipitated during aging, and the lowest hardness, due to a lower content of carbon in it (compared with the alloy 32NF) and carbide forming elements (compared with 34NFM alloy).

Thus, during aging the alloys precipitation hardening takes place, accompanied by increased hardness as a result of deposit dispersed carbides of alloying elements.

**The fifth chapter** discusses the features of thermal expansion of studied Invar alloys 32NF, 34NFM and 32NFK, as well as influence of heat treatment on the

value of coefficient of linear expansion and stability. Analysis of the dilatometric curve of heating for hardening up to 1200 and 1250 °C showed that they registered a few bends. In the temperature range from room temperature to 300 °C, the curve is not linear due to the manifestation of a magnetostrictive Invar effect "deterrent" thermal expansion. In the temperature range from 300 to 950-960 °C curve is linear character, which indicates the absence structural phase transitions. At a temperature of 950-960 °C depending on the alloy composition changes the angle of the curve, that indicating a slowing of thermal expansion associated with the development process the dissolution of carbide phase. Holding at a temperature of 1200 or 1250 °C results in a decrease in linear dimensions, indicating the dissolution of carbides. Subsequent rapid cooling, modeling quenching in water, fixing  $\gamma$ -solid solution without phase transformations, characterized by a sharp reduction in the linear dimensions due to thermal contraction.

Coefficient of linear expansion test on hardened alloys showed, that the coefficient of expansion for all the alloys in the range  $0.5 \times 10^{-6} \text{ K}^{-1} \leq \alpha \leq 3 \times 10^{-6} \text{ K}^{-1}$ .

In 32NFK alloy quenched from the temperature of 1250 °C, coefficient of linear expansion is very low  $\alpha = 0.91 \times 10^{-6} \text{ K}^{-1}$ , in spite of the saturation of the solid solution of carbon and vanadium, which can be explained by the effect of cobalt, which is being in the crystal lattice increases magnetostrictive effects. It should be noted, that after quenching coefficient of linear expansion values correspond to the technical requirements, but the mechanical properties do not satisfy them.

With aging in the range isothermal exposure for 1 hour at 650 and 700 °C, observed an increase in linear dimensions, that can be explained by the release of the carbide phase from the supersaturated solid solution by quenching fixed. It is known, that during aging the quenched samples carbon containing Invar

alloys, doped with carbide-forming elements, two competitive processes occur: the depletion of solid solution carbon atoms, resulting in a reduction in the volume and the precipitation of carbides, resulting in an increase in volume. In this case, the precipitation of carbides has dominant influence on the increase in specific volume, compared to the departure of the carbon atoms from the solid solution.

After aging coefficient of linear expansion all the alloys in the range  $0.5 \times 10^{-6} \text{ K}^{-1} \leq \alpha \leq 3 \times 10^{-6} \text{ K}^{-1}$  and complies with technical requirements.

However, the crystalline and magnetic domain structure of high-strength Invar alloys on the basis of the system Fe-Ni, additionally alloyed with carbon and carbide-forming elements, is in an unstable state, making them difficult to use for products which are required to size constancy of temperature changes in the operating conditions. To increase the stability of Invar alloys sizes typically used a special thermal treatment consisting in holding at 80 °C for 48 h. After a stabilizing treatment coefficient of linear expansion values, for all the alloys also were in the range defined by the specified requirements. Reheating to 150 °C for 1 h slightly changes the values of coefficient of linear expansion, that confirms stabilizing treatment action. Thus, the proposed thermal treatment the alloys should provide a high thermal stability.

On the experimental-industrial samples 34NFM, 32NF and 32NFK alloys under "Motovilikhinskiy plants" were tested heat treatment regimes, which allowed to get the properties complies with technical requirements. Analysis of the study results allowed to recommend 32NF alloys 34NFM 32NFK and for the organization of small-tonnage production of blanks from Invar alloy, which is confirmed by an act of implementation. The investigated alloys which have hardening heat treatment, superior to the properties to the nearest foreign analogues.

# SOMMARIO

Nell'introduzione l'attualità del tema della tesi, formulata l'obiettivo e obiettivi dello studio sono mostrati novità scientifica, il significato pratico del lavoro riflette le principali disposizioni per la difesa, la fiducia e il contributo personale dell'autore.

Il primo capitolo rivisto la letteratura nazionale ed estero, discute le cause fisiche di basso coefficiente di dilatazione lineare delle leghe Invar. Esempi di leghe di varie composizioni chimiche e il loro uso è considerato. Abbiamo analizzato le carenze di Invars classici e definito presupposti per migliorare le proprietà meccaniche del loro.

L'effetto della composizione chimica sulla struttura, proprietà meccaniche e speciali delle leghe Invar. E 'dimostrato che senza il trattamento termico non è possibile avere valori contemporaneamente bassi del coefficiente di dilatazione lineare e maggiori proprietà di resistenza. Analisi della letteratura mostra che ci sono solo alcuni dati sparsi sugli effetti del trattamento termico sulle proprietà meccaniche di alta resistenza leghe Invar con un basso coefficiente di dilatazione lineare. Non c'è consenso sull'effetto di temperatura e tempo parametri del trattamento termico non è disponibile.

E 'formulato l'obiettivo del lavoro e ha fornito il problema di ricerca.

Il secondo capitolo descrive i materiali e le tecniche sperimentali. Per indagare leghe invar sono stati selezionati sulla base del sistema di Fe-Ni, lega con elementi letteratura che assicuri l'indurimento di queste leghe di carbonio e carburo di formatura a causa della fase di carburo dispersa. Doping cobalto viene utilizzato per ridurre il coefficiente di espansione.

Le leghe sono stati fusi in un forno a induzione sotto vuoto a 60 kg lingotti, forgiati e poi laminati in barre. Trattamento termico dei campioni è stata

effettuata in un PL-20 laboratorio elettrico "Termodat" centralina e condotto nelle seguenti modalità:

- Tempra da una temperatura di 1200 1250 °C e raffreddato in acqua e olio;
- Il riscaldamento dei campioni temprati a temperature di 300, 500, 600, 650, 700 e 800 °C, tenuta per 1 ora e raffreddamento in aria;
- Riscaldamento e mantenimento dei campioni a 80 °C per 48 ore.

La microstruttura è stata esaminata al microscopio ottico Meiji Techno e microscopio elettronico a scansione sistema di microanalisi JEOL JSM-6490LV con INCA Energy 450. L'analisi quantitativa è stata effettuata utilizzando Thixomet sistema di analisi dell'immagine del computer PRO. La quantità di campione statistico costituito da 150 a 300 unità. errore di misura relativa non supera 5-7%.

Analisi diffrattometrica è stata effettuata su diffrattometro XRD-7000 SHIMADZU tubo radiogeno con anodo di cromo ( $\lambda = 2.285 \text{ \AA}$ ) ad una tensione di 40 kV e una corrente di 30 mA. Determinazione della composizione fase è stata realizzata in un pacchetto software International Centre for Diffraction dati PDF-2 di uscita 2014, con un database integrato in esso.

La durezza è stata misurata mediante Vickers secondo GOST 2999-75 sul universale durometro test M4S075G3 Emso piramide diamante indentazione sotto un carico di 29.42 N (3 kgf) e il tempo di esposizione sotto un carico di 15 secondi. Le caratteristiche di resistenza del materiale è stato determinato secondo GOST 1497-1484 in una prova di trazione campioni con porzione cilindrica attiva lunga 30 mm e 6 mm su una macchina di prova universale AG-IC 300 kN SHIMADZU.

Simulazione di trattamento termico e la determinazione coefficiente di dilatazione termica è stata eseguita su campioni da 10 mm di diametro e 80-90 mm di lunghezza Gleeble 3500 complicato, mantiene le sezioni trasversali

temperatura uniforme nel centro del campione in modalità di raffreddamento con diverse velocità di riscaldamento diverso o. Per le prove di dilatazione con sensore ad alta precisione, la cui risoluzione è 0.4 micron. Thermal regime test per determinare il coefficiente di espansione termica corrisponde GOST 14.080-78.

Il terzo capitolo presenta i risultati di studi di struttura leghe prima e dopo l'indurimento.

La struttura tondino laminato a caldo costituito da grani del substrato metallico e le particelle di seconda fase di diverse dimensioni. I risultati delle analisi di analisi microsonda hanno rivelato che gli spettri delle leghe a base di metallo si trovano in tutti i picchi di ferro, nichel, carbonio, e cobalto - in lega 32NKF, molibdeno - e una lega 34NFM di vanadio - e nelle leghe 32NFK 34NFM. -Analisi diffrattometrica portato leghe matrice identificazione come soluzione  $\gamma$ -solido con fcc lattice contenente questi elementi.

Mappa di distribuzione degli elementi chimici e spettri mikrorentgenovskie registrati dai singoli inclusioni dimostrare di essere concentrato carbonio, vanadio, molibdeno, titanio, e quasi non rilevabili ferro, nichel e cobalto, che ha permesso l'identificazione di tali particelle come carburi degli elementi di lega.

Oltre alla struttura di queste particelle grandi vengono osservate in cui l'analisi microsonda elettronica indica la presenza di una serie di elementi specifici di inclusioni non metalliche origine metallurgica. Queste particelle hanno preferibilmente una forma arrotondata, che conferma la loro separazione dalla massa fusa. La composizione chimica e la quantità di inclusioni non metalliche quando utilizzate per leghe fusori cinque opzioni disossidanti composizioni erano diverse. Sulla base dei risultati di analisi microscopica, microscopia elettronica e analisi microsonda elettronica, si è riscontrato che il più adatto è la composizione disossidante: 0.15% Mn raf, 0.35% NiMg



(0.15% Mg), 0.1% di Si Cr, 0.1% Sica, 0.06% di Al 0.07-0.1% di Tispugna, che fornisce meno forma, più piccolo e più favorevole di inclusioni non metalliche origine metallurgica.

Dopo tempra dal 1200 e 1250 °C in acqua e in olio nel grano fisso particelle di carburo struttura base metallica di dimensioni diverse, con un mezzo di raffreddamento di qualsiasi effetto significativo sulla natura della struttura non ha.

Spiegazione diffrazione ottenuti mediante analisi ai raggi X dimostrava che la base di metallo delle leghe, nonché nella condizione iniziale laminati a caldo ha FCC lattice, ossia  $\gamma$  polimorfico  $\rightarrow$  trasformazione  $\alpha$  durante la tempra è assente. Aumentando la temperatura di riscaldamento per raffreddamento si osserva aumento della granulometria e riducendo il numero delle particelle di carburo rispetto allo stato iniziale, come confermato da analisi quantitativa.

Metodo dilatometrico analisi stabilito che la dissoluzione della fase di carburo durante il riscaldamento per tempra inizia ad una temperatura di 950-960 °C e continua per la tenuta isotermica, come dimostrano le inflessioni caratteristici delle curve dilatometriche delle leghe.

Studi radiografici hanno dimostrato che i modelli di diffrazione di campioni bonifica di tutte e tre le leghe, uno spostamento dei picchi caratteristici riflessi da piani cristallografici rispetto allo stato iniziale. parametri reticolari modifica è stata trovata una soluzione  $\gamma$ -solida sulla base dei risultati dell'analisi calcolati diffrazione di raggi X, che indicano un cambiamento nella lega soluzione  $\gamma$ -solida durante l'indurimento dovuto al passaggio ad esso e gli atomi di carbonio degli elementi di lega della fase carburo, disciolti sotto riscaldamento.

Il quarto capitolo presenta i risultati di studi sulla struttura e le proprietà meccaniche delle leghe Invar sottoposti dopo tempra di calore. Un aumento

della temperatura da 300 a 650-700 °C è accompagnata da un aumento della durezza e ad alte temperature fino a 800 °C provoca il declino.

La durezza e resistenza alla trazione dopo riscaldamento dei campioni precedentemente bonificato da alta temperatura 1250 °C, è stata superiore rispetto alle proprietà di campioni bonifica da una temperatura inferiore di 1200 °C. In questo caso il mezzo di raffreddamento non ha alcun effetto significativo sulla durezza dei campioni dopo il calore, in modo che il trattamento termico come acqua mezzo di raffreddamento può essere raccomandato come più ecologico.

Il più grande rinforzo nelle leghe 34NFM (durezza 300 HV, la resistenza alla trazione  $R_m = 870 \text{ N/mm}^2$ , snervamento  $\sigma_{0.2} = 780 \text{ N/mm}^2$ ) e 32NF (durezza 400 HV, la resistenza alla trazione  $R_m = 1150 \text{ N/mm}^2$ , snervamento  $\sigma_{0.2} = 1030 \text{ N/mm}^2$ ) temperatura raggiunta dalla tempra da 1250 °C seguito da riscaldamento a 700 °C. La più grande rinforzo per lega 32NFK (durezza 250 HV, resistenza alla trazione  $R_m = 800 \text{ N/mm}^2$ , snervamento  $\sigma_{0.2} = 720 \text{ N/mm}^2$ ) è realizzato con la tempra dalla temperatura di 1250 °C seguito da riscaldamento a 650 °C.

Dopo il riscaldamento, le particelle grossolane vengono osservate le leghe metalliche di base non completamente fusi durante il riscaldamento per il raffreddamento, e le particelle disperse dimensioni fra 70 e 320 nm. L'analisi quantitativa mostra che la proporzione relativa delle particelle grossolane dopo il campione riscaldamento temprato non è cambiato rispetto allo stato indurito, e la quantità di particolato aumentando la temperatura di riscaldamento da 300 a 700 °C aumentato. Ciò dimostra l'assegnazione delle particelle di decadimento soluzione satura solido ottenuto dalla tempra. Electron metodo microsonda, le particelle sono stati identificati come carburi contenenti vanadio. La formazione di fasi intermetalliche, è stato rilevato

caratteristica del sistema Fe-Ni, confermata dai risultati di analisi a raggi X, e carburi formula può essere descritto come VC ( $V_4C_3$ ).

Nell'interpretazione pattern di diffrazione ottenuti con l'analisi ai raggi X ha rivelato che dopo l'invecchiamento dei campioni di lega temprati, uno spostamento caratteristici picchi di riflessione. Il parametro reticolare calcolato rispetto allo stato indurito di cambiamento che indica un cambiamento in lega di soluzione di  $\gamma$ -solida durante l'invecchiamento a causa della transizione degli atomi di carbonio ed elementi carburo formano nella fase di stand-carburo. Metodo dilatometrico analisi cambiamenti caratteristici dell'angolo delle curve sono stati registrati, che è anche evidenziato dal assegnazione di particelle di carburo disperse durante l'invecchiamento.

Più alta è la temperatura di riscaldamento per il raffreddamento fornire più completa dissoluzione del carburo di partenza particelle maggiore saturazione del carbonio soluzione solida e elementi di lega, e, di conseguenza, un maggiore effetto indurimento per precipitazione in suo decadimento, che spiega la maggiore durezza. Riduzione della durezza all'aumentare della temperatura di invecchiamento a 800 °C di coagulazione è spiegato particelle di carburo, come dimostrato da studi microstrutturali.

In molibdeno lega 34NFM è presente soprattutto in grandi carburi, che non completamente dissolvono quando riscaldato per l'indurimento, soluzione  $\gamma$ -solido leggermente saturo di molibdeno, e la proporzione di carburi molibdeno dispersi, rilasciato durante il successivo riscaldamento è piccola. Pertanto, drogaggio di molibdeno nel ridurre il contenuto di carbonio e vanadio nel 34NFM lega era meno efficace per il rinforzo precipitazione rispetto solo il vanadio 32NF drogata: la massima durezza della lega durante 34NFM invecchiamento era 100 HV, e la resistenza alla trazione - 450 N/mm<sup>2</sup> seguito, di lega di 32NF.

Il 32NFK lega osservato minor numero di particelle di carburo disperse precipitate durante l'invecchiamento, e la durezza bassa, a causa di un minor contenuto di carbonio in esso (rispetto al 32NF lega) ed elementi formando carburo (rispetto lega 34NFM).

Così, dopo invecchiamento queste leghe precipitazione indurimento avviene, accompagnato da un aumento di durezza per effetto di carburi disperse di elementi di lega.

Il quinto capitolo illustra le caratteristiche di espansione termica delle leghe Invar studiati 32NF, 34NFM e 32NFK, così come effetto del trattamento termico sui valori del coefficiente di dilatazione termica e stabilità.

L'analisi della curva di dilatometrico di riscaldamento per l'indurimento fino a 1200 e 1250 °C ha mostrato che si sono registrati alcuni intoppi. Nell'intervallo di temperatura da temperatura ambiente a 300 °C, la curva non è lineare a causa della manifestazione di un effetto magnetostrittivo Invar "deterrente" espansione termica. Nell'intervallo di temperatura dalla curva 300 a 950-960 °C è di natura lineare, indicando transizioni di fase strutturali. Ad una temperatura di 950-960 °C a seconda della composizione della lega cambia l'angolo della curva, che indica un rallentamento della dilatazione termica associata al processo di sviluppo dissoluzione della fase carburo. Tenendo ad una temperatura di 1200 °C o 1250 provoca una riduzione delle dimensioni lineari, indicando la dissoluzione di carburi. Successivamente quenching rapido raffreddamento in acqua e modellazione fissa trasformazioni di fase gamma-soluzione solida, senza perdite, caratterizzato da una drastica riduzione delle dimensioni lineari a causa della contrazione termica.

Prova CTE leghe indurite hanno mostrato che il coefficiente di espansione per tutte le leghe nell'intervallo  $0.5 \times 10^{-6} \text{ K}^{-1} \leq \alpha \leq 3 \times 10^{-6} \text{ K}^{-1}$ .

In lega 32NFK bonificato dalla temperatura di 1250 °C, il coefficiente di espansione termica è estremamente basso valore di  $\alpha = 0.91 \times 10^{-6} \text{ K}^{-1}$ , nonostante la saturazione di una soluzione solida di carbonio e vanadio, che può essere spiegato dall'effetto di cobalto, che sono in reticolo cristallino aumenta effetti magnetostrittivi. Vale la pena notare che dopo i valori indurimento del coefficiente di dilatazione termica corrispondono ai requisiti tecnici, ma le proprietà meccaniche non li incontrano.

Con l'invecchiamento vanno esposizione isoterma per 1 ora a 650 e 700 °C, un aumento di dimensioni lineari, che può essere spiegato dal rilascio della fase di carburo dalla soluzione solida sovrassatura con la tempra registrata. È noto che durante l'invecchiamento dei campioni temprati carboniosi leghe invar drogati con elementi di carburo di formazione, si verificano due processi competitivi: la deplezione di atomi di soluzione di carbonio solido, con una conseguente riduzione del volume e la precipitazione di carburi, causando un aumento di volume. In questo caso, la precipitazione di carburi ha influenza dominante aumento di volume specifico rispetto al trattamento degli atomi di carbonio della soluzione solida.

Dopo l'invecchiamento del coefficiente di dilatazione termica delle leghe è nel campo di  $0.5 \times 10^{-6} \text{ K}^{-1} \leq \alpha \leq 3 \times 10^{-6} \text{ K}^{-1}$  ed è conforme alle specifiche.

Tuttavia, la struttura del dominio cristallina e magnetico ad alta resistenza leghe Invar sulla base del sistema Fe-Ni, inoltre legato con carbonio ed elementi carburo di formazione, è in uno stato instabile, rendendole difficili da usare per i prodotti che devono dimensioni costanza delle variazioni di temperatura delle condizioni operative. Per aumentare la stabilità di Invar leghe dimensioni, di solito si utilizza uno speciale trattamento termico, che consiste nell'estratto a 80 °C per 48 ore. Dopo stabilizzanti valori trattamento del coefficiente di espansione termica per tutte le leghe erano nell'intervallo definito dai requisiti specificati ( $0.5 \times 10^{-6} \text{ K}^{-1} \leq \alpha \leq 3 \times 10^{-6} \text{ K}^{-1}$ ). Riscaldare

a 150 °C per 1 ora, leggermente modifica i valori di coefficiente di dilatazione termica, confermando le fasi di lavorazione stabilizzanti. Quindi, il trattamento termico proposto delle leghe dovrebbe fornire una elevata stabilità termica.

Sulle sperimentale-industriale leghe campioni 34NFM, 32NF e 32NFK sotto fabbrica "MZ" sono stati testati i regimi di trattamento termico, che diedero le proprietà condizioni specificate. L'analisi dei risultati dello studio hanno permesso di raccomandare 32NF leghe 34NFM 32NFK e per l'organizzazione della produzione su piccola stazza dei grezzi in lega Invar, che viene confermata da un atto di attuazione.

Le leghe di prova sottoposti ad un trattamento termico di indurimento, superiori alle proprietà o almeno non inferiori alla prossima controparti estere.

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# INTRODUCTION

Invar alloys is a group of precision alloys with a given temperature coefficient of linear expansion (CTE) [1]. A low CTE in the various areas of temperatures, as well as mechanical, technological and corrosion properties allow using Invar alloys as a structural material for the instrument parts, which are required to have constant size at temperature changes in the operating conditions [2-5]. Products of the aerospace industry, laser parts, measurement and metrological equipment, spectrometers parts and gyroscopes, units of various fasteners, lathes, jig boring and grinding machines rails are made of Invar alloys [6-9].

Classic Invar compositions based on Fe-Ni 36% systems have a hardness of about 120 HV, ultimate strength of 440-480 MPa and CTE  $\alpha_{20-100} \leq 1.2 \times 10^{-6} \text{K}^{-1}$  [10]. Meanwhile, the modern high-tech industries that use Invar alloys for the manufacture of critical parts make new demands arising from the need to improve mechanical properties while maintaining low values of the coefficient of linear expansion. The Invar alloys of traditional chemical composition are not able to provide the necessary level of mechanical properties even after the hardening heat treatments [10].

Introduction of alloying elements into an alloy based on Fe-Ni can influence the mechanical, technological and special properties of Invar alloys. [11-19]. A number of studies have shown that materials of this type may be hardened due to the precipitation hardening with separation of intermetallic phases while alloying by elements that contribute to the formation of intermetallic compounds during thermal aging [14, 15]. Introduction of carbon provides solid solution hardening and extends the temperature range in which the lower values of CTE are saved [16]. Introduction of strong carbide forming elements improves the strength properties due to hardening of carbide. Very effective

additives in this regard are tungsten, titanium, vanadium and molybdenum [20-22]. However, well known alloys of this type have a relatively high coefficient of linear expansion  $\alpha \geq 3 \times 10^{-6} \text{K}^{-1}$ .

Recently, new high-invar alloys based on Fe-Ni system have been developed, which differ from the world analogs by minimum values of CTE ( $\alpha \leq 3 \times 10^{-6} \text{K}^{-1}$ ). Introduction of carbon, cobalt and carbide forming alloying elements provides hardening due to separation of carbide phases. Research aimed at the development of industrial technologies of blanks production from these innovative high-strength Invar alloys have been conducted by scientists of "Nosov Magnitogorsk State Technical University" in cooperation with the specialists of "Motovilikhinskiy plants" for several years [23-26]. In accordance with the specifications of an ultimate strength of alloys should be at least  $800 \text{ N / mm}^2$  and the coefficient of linear expansion in the temperature range from  $20$  to  $150 \text{ }^\circ \text{C}$  must be between  $0.5$  to  $3 \times 10^{-6} \text{ K}^{-1}$ . However, until recently, in scientific literature there were only a few scattered data on the effect of heat treatment on the value of CTE and mechanical properties of high - strength Invar alloys with a low coefficient of thermal expansion. Therefore, an urgent task is the study of features of the structural changes course during heat treatment and their influence on the properties of Invar alloys that provide improved strength characteristics while maintaining a low CTE, meeting the needs of high-tech industries in the modern materials for special purposes.

The work has been carried out in the framework of an integrated project to create a high-tech production, performed with the participation of the Russian higher educational institution (contract № 02.G25.31.0040) and the strategic development program of the University for 2012-2016. (Ministry of Education for competitive support of strategic development programs). The purpose and objectives of the work correspond to priority directions of development of

science, technology and engineering in the Russian Federation "Industry of Nanosystems", approved by Presidential Decree N 899 of July 7, 2011, as well as to the tasks implemented within the framework of officially recognized in Russia Technological Platform "Technology of Metallurgy and new materials (paragraph 21 Materials and technologies of metallurgy) ".

**The purpose of the work** is the definition of the modes of heat treatment for improving the strength values while maintaining a low coefficient of linear expansion of Invar alloys, of the Fe-Ni-C system, alloyed with cobalt, vanadium and molybdenum.

To achieve this goal, the following **main objectives** have been set and solved:

1. To investigate patterns of influence of temperature and time of heating conditions for quenching and cooling fluid on the structural characteristics and mechanical properties of Invar alloys of the Fe-Ni-C, additionally alloyed with cobalt, molybdenum and vanadium.
2. To determine the effect of heat treatment conditions at heating hardened Invar alloys on their structure and mechanical properties.
3. To set the behavior of the temperature coefficient of linear expansion in the high-strength Invar alloys under thermal exposure.
4. To give guidance on heat treatment regimes of Invar alloys to provide increased levels of strength (Ultimate tensile strength (UTS)  $\geq 800$  H/mm<sup>2</sup>, the hardness of HV 250-400) and maintaining the thermal expansion coefficient in the low range  $\alpha \leq 3 \times 10^{-6} \text{K}^{-1}$ .

**Scientific novelty:**

1. Quantitative and qualitative patterns of structure formation and obtaining the properties of new Invar alloys 32NF 34NFM and 32NFK with improved performance characteristics, describing the effect of tempering regimes and subsequent aging on the mechanical properties experimentally obtained.

2. It has been established that the maximum hardening is provided by precipitation hardening with release of resistant carbides of alloying elements during thermal treatment, which consists in quenching from 1250 °C in water, followed by aging at 700 °C for 1 h and stabilization at 80 °C for 48 h. It provides: for 32NF alloy hardness is 400 HV, UTS = 1150 H/mm<sup>2</sup>,  $\sigma_{0.2}$  = 1030 H/mm<sup>2</sup>,  $\alpha$  =  $1.3 \times 10^{-6}$  K<sup>-1</sup>, for 34NFM alloy hardness is 300 HV, UTS = 870 H/mm<sup>2</sup>,  $\sigma_{0.2}$  = 780 H/mm<sup>2</sup>,  $\alpha$  =  $2.4 \times 10^{-6}$  K<sup>-1</sup>. 32NFK cobalt alloy for the heat treatment regime is quenched from 1250 °C in water, followed by aging at 650 °C and stabilizing at 80 °C for 48 hours and it provides hardness 250 HV, UTS = 800 H/mm<sup>2</sup>,  $\sigma_{0.2}$  = 720 H/mm<sup>2</sup>,  $\alpha$  =  $1.67 \times 10^{-6}$  K<sup>-1</sup>.

3. The character of CTE changes and its stability during thermal impact has been revealed, proving that the recommended mode of heat treatment of high-Invar alloys 32NF, 34NFM and 32NFK provides low values of coefficient of linear expansion ( $\alpha \leq 3 \times 10^{-6}$  K<sup>-1</sup>) and their stability only after special heat treatment.

### **Practical significance:**

1. It has been shown that hardness (up to 250-400 HV) and UTS (up to 800-1150 N / mm<sup>2</sup>) can be increased almost twice which is achieved by quenching from the temperature of 1250 °C followed by aging of the quenched samples at 650-700 °C in the carbonaceous Invar alloys, alloyed with vanadium and molybdenum, compared with the classical Invars. At the same time low values of the coefficient of linear expansion ( $\alpha < 3 \times 10^{-6}$  K<sup>-1</sup>) have been maintained.

2. Sizes stability of products made of invar alloys of the investigated compositions in the temperature range of 20-150 °C has been provided by an additional stabilizing treatment consisting in holding them at 80 °C for 48 hours.

3. It has been established that a satisfactory chemical composition from the standpoint of forming and the amount of non-metallic inclusions most suitable for the invar alloys under investigation is the deoxidized mixture of the following composition: 0.15% Mn<sub>ref</sub>, 0,35% NiMg (0,15% Mg), 0,1% Si<sub>cr</sub>, 0,1% SiCa, 0,06% Al and 0,07-0 1% Ti<sub>sponge</sub>.

4. Recommended for alloys 32NF, 34NFM, 32NFK heat treatment regimes have been used in conditions of “Motovilikhinskiy plants“ for the organization of the small-tonnage production of blanks made of Invar alloys, different from the world analogues by improved performance characteristics and satisfying the needs of high-tech industries in modern materials for special purposes, as confirmed by the act of introduction.

**The author’s personal contribution.** All the presented in the thesis experimental studies, as well as the processing of the experimental data had been carried out by the author himself or with the direct participation of the author. The author was directly involved in the development of ideas, setting of goals and objectives of the research, arranging experiments, discussions and formulation of the results and writing of the articles on the topic of the thesis.

**Degree of authenticity** has been confirmed by the use of modern research methods on the structure and properties of Invar alloys samples. These results do not contradict the current theoretical understanding of the processes occurring during the thermal impact on the alloys of the system Fe-Ni, and they have been confirmed in the manufacture of commercial batches of work-pieces of Invar alloys in the conditions of “Motovilikhinskiy plants“.

# **CHAPTER 1**

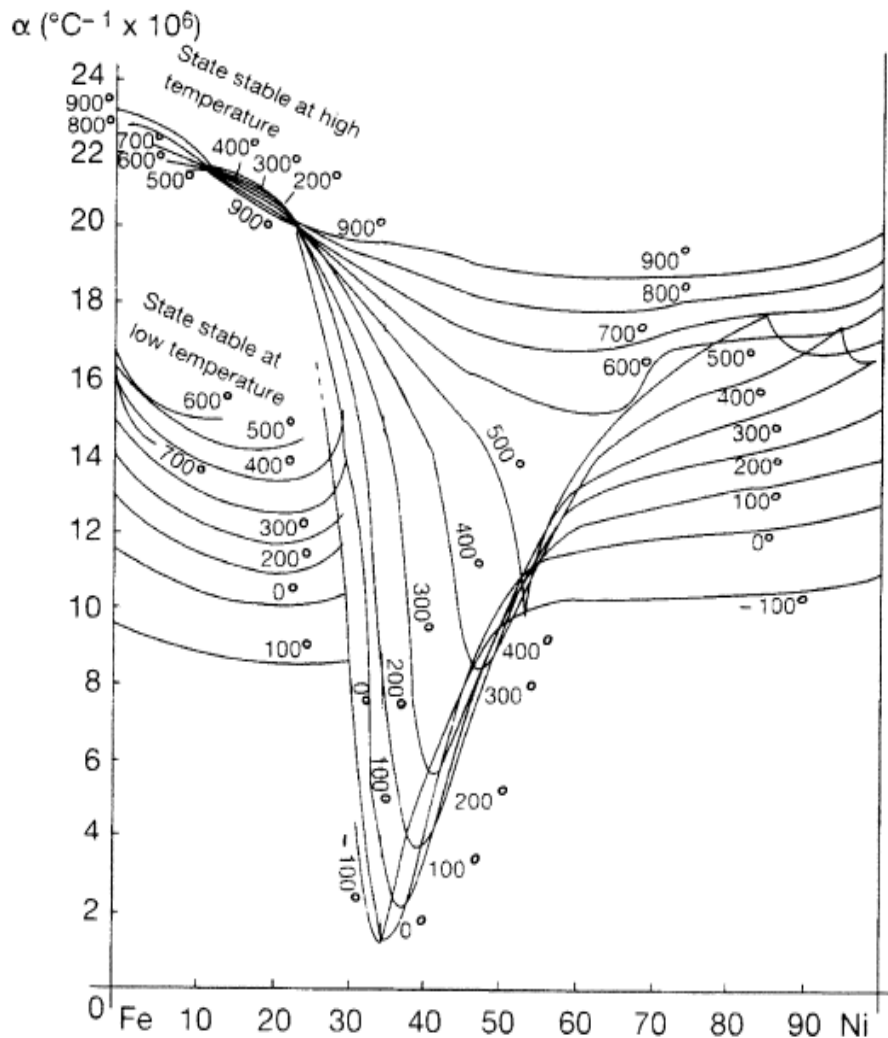
## **ANALYSIS OF STRUCTURE FORMATION AND PROPERTIES OF INVAR ALLOYS**

### **1.1. Characteristics of Invar alloys and their use in engineering**

Invar alloys is a group of precision alloys with a given temperature coefficient of thermal expansion (CTE). The first Invar alloy containing 36 atomic percent of nickel (the left content is iron), was discovered by Charles Edouard Guillaume (Ch. Guillaume) in 1896 in Paris [1]. He was awarded the Nobel Prize for this discovery in physics in 1920.

Various researchers have shown that abnormally low spreading factors are observed only within a certain range of nickel concentrations [5, 27]. Figure 1.1 shows this relationship. The minimum CTE is observed when the content of nickel is 36%. If nickel content is less than 25% formation of concentration non-homogeneities and the regions of short range order is complicated, and, hence, the incentive to increase the strength properties is reduced, besides if the content of nickel is less than 25% the resistance of the alloy decreases to  $\gamma \rightarrow \alpha$  martensitic transformation. The  $\alpha$ -phase formation due to martensitic transformation deteriorates the mechanical properties and leads to a significant increase in thermal expansion. When the content of nickel in the alloy is more than 48% such electronic and atomic structure is formed, which no longer provides low thermal expansion coefficient. This is due to the fact that at higher nickel content (over 48%) larger concentration non - homogeneities are formed [28, 29].

Classic Invar alloy has a nominal composition of Fe-36% Ni and is characterized by a fully austenitic structure, under normal conditions, and has a very low coefficient of thermal expansion ( $\alpha \leq 3 \times 10^{-6}K^{-1}$ ) within a certain range temperatures than most metal materials which have  $\alpha \approx 10 - 20 \times 10^{-6}K^{-1}$ . So for example the coefficients of thermal expansion of commercially pure nickel and iron are approximately equal to  $\alpha \approx 12 \times 10^{-6}K^{-1}$ .



**Fig. 1.1** Dependence of CTE system Fe-Ni from the nickel content at various temperatures [27]

Considering the thermal expansion at the atomic level, volume increase of any material during heating can be explained by an increase of the distance between atoms. The more the energy of atomic bonds is the lower CTE is [8]. For example, ceramics with relatively high energy of interatomic bonds have a lower coefficient of expansion than the metal and polymer materials [9]. This is reflected in Table 1.1.

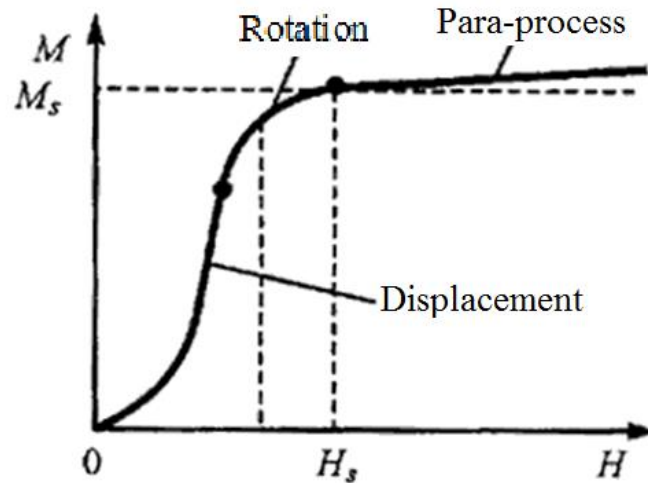
**Table 1.1** Coefficients of thermal expansion of different materials [9]

Material	CTE, $10^{-6}K^{-1}$
Aluminum	23.6
Copper	17.0
Gold	14.2
Iron	11.8
Nickel	13.3
Silver	19.7
Tungsten	4.5
1025 Steel	12.0
316 Stainless Steel	16.0
Brass	20.0
Quartz glass	0.4
Glass BK7	7.1
Borosilicate glass	3.3
The polymers (plastics)	~100-200

The understated value of the coefficient of linear expansion of Invar alloys has a ferromagnetic nature and is due to the high magnetostriction of the para-process, i.e., due to changes in dimensions of a ferromagnetic at its



magnetization. In the field of technical magnetization, where the magnetic field is less than the technical saturation point ( $H < H_s$ ) the magnetostriction is linear and in the field of the para-process ( $H > H_s$ ) it has a volumetrical character (Figure 1.2) [30, 31].



**Fig. 1.2** The basic magnetization curve

In all ferromagnetic materials, except for the type of Invar alloys, the magnetization  $M_s$  in the area of the para-process with the field growth remains practically unchanged (the dashed line in Figure 1.2). In the invar type alloy magnetization in this region increases (solid line in Figure 1.2) resulting in additional electron spin moments orientation somewhat disoriented by the thermal motion, and causes large magnetostriction phenomenon [32-35].

The same phenomena occur under the influence of the internal magnetic field of the ferromagnetic: in the absence of an external field the shape and size of the domain are deformed by magnetostriction [36, 37]. The true size is detected only when heated to the temperature above the Curie point, when all the magnetostrictive strain are eliminated in connection with the transition to the paramagnetic state. Upon cooling to temperatures below the Curie point the

linear magnetostriction distorts the shape of the domain, extending it in the direction of the spontaneous magnetization vector. The volume magnetostriction increases the size of the domain [38-40].

In the crystals of the ferromagnetic, except for the alloys of the Invar type, magnetostriction, which arose due to the internal field, is not detected, as the volume magnetostriction in them is small, and the linear one is compensated by the deformation of domains in different directions. In the alloys of the Invar type the sizes of a ferromagnetic are increased, as they have a large volume component of the magnetostriction [31, 41, 42].

Temperature coefficient of linear expansion of ferromagnetic is generally defined by the formula [43]:

$$\alpha = \alpha_0 - \Delta,$$

where  $\alpha_0$  – is a normal linear expansion coefficient that depends on the binding energy of the atoms;

$\Delta$  – is a ferromagnetic component of the coefficient of linear expansion, which is conditioned by the volume magnetostriction para-process.

When heated above the temperature of the Curie point, the ferromagnetic component of the coefficient of thermal expansion disappears due to the transition of the alloy to the paramagnetic state of the alloy, and the CTE increases sharply. All the above said explains the anomalous values of the CTE in Invar alloys [44-46].

The low value of the CTE in various areas of temperatures as well as mechanical, technological and anti-corrosive properties allows using the Invar alloys as construction materials for parts of devices, in which dimensional stability with varying the temperature is required in operation [47, 48]. Invar alloys are widely used in precision machine tools, namely, attachment points of different fasteners; guides of lathes, jig boring and grinding machines, laser equipment, cryogenic equipment [49, 50], the products of the measuring,

control - alignment and metrology equipment, including parts of spectrometers, measuring machines and stands are made [51].

Some brands of Invar alloys with sufficient mechanical properties are used for the manufacture of molds for different materials, such as carbon fiber, for the formation of which machining attachments with a low CTE at higher temperatures, and in astronomical equipment (frames of telescopes) are required. The alloys the Invar interval of which is in the region of negative temperatures, are actively applied in cryogenic technology, for example, for parts in installations for liquefaction and transportation of natural gas.

Invar alloys worked well for opto-mechanical systems [52], the parts of which should have constant sizes when the temperature is changed. The wavelength of light in the visible part of the spectrum for optical systems is approximately 0.5 microns. Accordingly, the requirements for the units and parts for these systems imply dimensional stability in that range.

A great group of Invar alloys consists of alloys for brazing and welding with glass [53]. The compositions of these alloys are chosen so as to match the CTE of the alloy with that of the material with which the connection is made over the entire range of temperatures up to the softening point of the glass. This ensures that the junction during heating and cooling (during manufacture and in operation) and obtaining tight connection. The main representative of this group is the alloy 29NK (Kovar) has the same CTE as the heat-resistant glass, tungsten and molybdenum. In this alloy, some amount of nickel is replaced by cobalt, which increases the temperature of the Curie point, and extends the scope of application up to 420 ° C. Under the same temperatures the heat-resistant glass begins to soften. The alloy is ductile and is well treated by pressure, so it replaced less plastic tungsten and non-heat resistant molybdenum in the electrical vacuum operations.

The alloy 47ND (platinite) refers to a group of alloys having the same CTE as platinum and non-heat resistant glass. It is used for welding and soldering with these glasses in the electric vacuum industry. Due to the high content of nickel the alloy has a high soldering temperature of the Curie point.

The alloy 33NK, which is an analogue of Kovar, but with a high content of nickel is used for ceramics. For such soldering very precise coincidence of expansion coefficients is not required, which simplifies the manufacturing technology of this alloy production.

As a temperature controller in the instrument engineering bimetallic plates welded from two materials with different values of the coefficient  $\alpha$  are used. For this purpose the Invar alloy 36N is usually used, because it has a minimum value of the coefficient  $\alpha$ , and the alloy with 25% Ni, which has a very large factor ( $\alpha \approx 20 \times 10^{-6} \text{K}^{-1}$ ). When heated, the bimetal plate is strongly curved and closes (or opens) the electrical circuit.

For the first time in 1931 Masumoto, having added 5% of cobalt into the Invar alloy of Fe 64% - 31% of Ni, received a superinvar alloy [54]. The coefficient of expansion of the superinvar can reach the values close to zero, but this alloy has a relatively narrow temperature range in which the CTE will be minimal [55-57].

These effects are due to the presence of cobalt, which being in the crystalline lattice on principle of substitution preserves low values of CTE [58, 59]. The sharp change in coefficient of expansion depending on the temperature did not allow to find wider application for this type of Invar alloy. Table 1.2 shows the values of CTE of Invar alloys in different temperature ranges, which are most commonly used in various industries.

**Table 1.2** Temperature coefficients of linear expansion of different Invar alloys in various temperature ranges depending on the heat treatment conditions [10]

Alloy grade	Temperature coefficient of linear expansion ( $\alpha \times 10^{-6}K^{-1}$ ), in the temperature range °C							Heat treatment regime
	20-80	20-100	20-300	20-400	20-450	20-500	20-800	
36N	No more than 1.2	-	-	-	-	-	-	Hardening of blanks with temperature $(840 \pm 10) ^\circ C$ , cooling in water, tempering the samples at the temperature of $(315 \pm 10) ^\circ C$ , holding 1 hour, cooling with the furnace.
32NKD	-	No more than 1.0	-	-	-	-	-	
30NKD 30NKD-VE			3.3-4.3	3.8-4.6		5.9-6.7		Annealing of blanks or samples in hydrogen, vacuum or protective atmosphere at a temperature of $(960 \pm 20) ^\circ C$ , 1-hour exposure Cooling. with an oven to $200 ^\circ C$ at a rate not exceeding $10 ^\circ C / min$
29NK 29NK-VE			4.6-5.5	4.6-5.2		5.9-6.4		
29NK-1 29NK-VE-1			4.8-5.3	4.7-5.1		6.0-6.4		
38NKD 38NKD-VE			7.0-7.9	7.0-7.9		8.2-8.9		
33NK 33NK-VE			7.4-8.4	7.0-7.6		7.3-7.9	10.4-11	
47NHR			8.4-9.0	9.4-10	-	10-11	-	
47NH			7.2-8.1	7.4-8.0	7.8-8.7	8.6-9.3	-	
48NH			8.4-9.2	8.4-9.0	8.6-9.4	9.1-9.7	-	

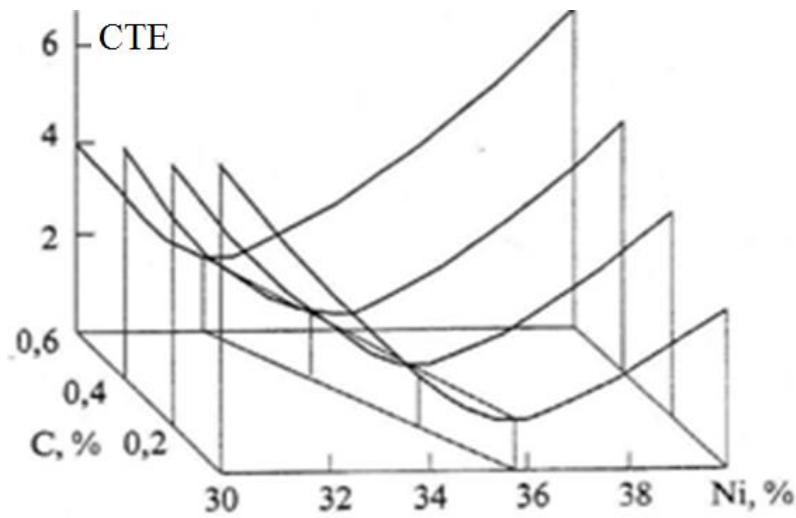
## **1.2. Influence of chemical elements on the structure and properties of Invar alloys**

Thermal and mechanical properties of Invar alloys mainly depend on the chemical composition. The addition of alloying elements in an alloy based on Fe-Ni can influence the mechanical, technological and special properties of Invar alloys, as evidenced by the works of many researchers [60-62]. The classic Invar alloy, containing 36% of nickel, has a hardness of about 120 HV, ultimate strength of 440-480 MPa and the CTE  $\alpha_{20-100} \leq 1.2 \times 10^{-6} \text{K}^{-1}$  [30].

A significant effect on both the mechanical and thermal properties of invar alloys is made by carbon [63, 64]. It may occur in the crystal lattice in a structurally free state in the form of graphite [65] or on the basis of introduction providing for the solid solution hardening, consolidation of dislocations at relatively low temperatures of around 100 °C, and, moreover, can extend the temperature range over which lower values of CTE are retained. Also, carbon may be present in the alloy in the form of chemical compounds, and the introduction of strong carbide forming elements improves the strength properties due to the carbide hardening without substantially reducing the characteristics of invar alloys [12, 17-19, 21, 66-68]. Regardless of the location of carbon in the alloy, it affects the value of the CTE negatively, increasing its value [64]. This relationship is shown in Figure 1.3.

A separate group of Invar alloys constitute the alloys with improved casting properties [15, 16, 29]. The peculiarity of the chemical composition is an increased content of carbon and up to 2% cobalt and 20%, respectively [69]. The carbon in these alloys is released from a supersaturated solid solution in the form of graphite and absorbs excess stresses occurring during casting. Cobalt plays the same role as in superinvar alloys, that is it lowers the coefficient of linear expansion. In the work [70] superinvar alloys of the system

Fe-Ni-Co carbon was added to improve casting properties. As a result, the carbon in the alloy was allocated evenly throughout the volume of the section in the form of graphite in finely dispersed form, and the CTE, even after graphitizing heat treatment remained within the corresponding to the definition of the minimum coefficient  $\alpha_{20-100} \leq 1.5 \times 10^{-6} \text{K}^{-1}$ .

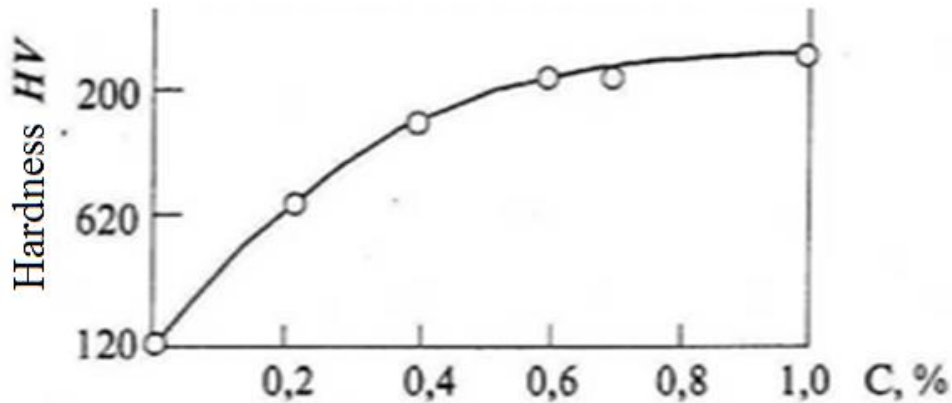


**Fig. 1.3** Changes in CTE in the range from 20 to 100 ° C depending on the concentration of nickel and carbon in the alloys of the Fe-Ni-C [4]

Introduction of carbon into the Invar alloy increases the stability of the FCC lattice of the structure to the martensitic transformation. Additionally, carbon in a solid solution is a source of local distortion. With an increase of its content hardness in the alloys increases (Figure 1.4) which is caused by distortion of the crystal lattice, increasing the friction forces that impede the movement of dislocations.

Doping of carbon leads to a decrease in the stacking fault energy, impedes lateral sliding, thereby causing hardening [71]. The emergence of these distortions also promotes the processes of redistribution of atoms to form sub micro-heterogeneities that is the areas, rich and poor with nickel. The share of

regions rich with nickel increases with increasing of carbon and nickel concentrations in the alloy. As a result, the domain structure is created, in which each of the magnetic domains has a magnetostrictive effect. This structure ensures formation of invar properties [6].



**Fig. 1.4** Change in hardness according to carbon content in alloys of Fe-34% Ni-C [4]

During the operation or heat treatment due to the release of carbon from the solid solution the values of the CTE change [72]. This is due to the change in the lattice parameter and the magnetostriction paraprocess, so maintaining low values of the CTE the carbon content in the solid solution should be as small as possible, but small carbon additives in iron - nickel alloys expand the temperature range in which a low value of the CTE is retained [4, 6].

The presence of carbon in the alloy containing carbide forming elements should contribute to the formation of stable carbides [17], such as vanadium carbide (1800-2200 HV) and molybdenum carbide (1200-1300 HV) [73]. The formation of such carbides causes hardening of alloys. However, the coefficients of expansion of most carbides is significantly higher than the CTE of Invar alloys, but if the volume of their share in the structure is small, it does



not cause a sharp rise in the CTE. So in the article [18] it was shown that, when introduced into a carbonaceous Invar alloy of various carbide-forming elements in all the cases the CTE retains minimum values of  $\alpha \leq 3 \times 10^{-6} \text{K}^{-1}$ .

One of the important alloying elements Fe-Ni-C of the invar alloys is vanadium, which is introduced to improve mechanical properties, mainly to improve the strength and yield strength [19, 20]. It is also known that vanadium increases the Curie point in invar alloys [74]. The introduction of vanadium into the carbon containing Invar alloys contributes to the formation of carbides [21, 68]. In the Fe-V-C system, according to most scholars a carbide composition of VC (or  $\text{V}_4\text{C}_3$ ) is formed with a cubic lattice in which a portion of seats allocated for carbon atoms can be not filled and the ratio of Me: C, varying from 1: 1 to 1: 0.75, describes the boundary of the existence of carbide. [75, 76].

Due to the fact that the formation of vanadium carbides occurs homogeneously throughout the volume of the grain, it contributes to strengthening of the alloys while maintaining a sufficiently high level of ductility. In addition, the introduction of vanadium inhibits the growth of the grain at a content above 0.01% if heating the alloys for hardening and thereby it prevents the embrittlement of alloys [77]. When the content of vanadium in the alloy is less than 0.01% its effect on the grain growth and, consequently, the mechanical properties is insignificant. When the content of vanadium is greater than 3% the share of the carbide phase in the austenitic structure is increased and there is a significant increase in the CTE then the alloy almost loses the Invar properties [6, 76].

Another carbide forming element effective for Invars alloying is molybdenum. In recent years, many researchers have investigated the impact of molybdenum on the Invar alloys as an alloying element that forms carbides persistent [17, 78-80]. The alloying by this element of carbon containing Invar alloys allows receiving carbides of the type  $\text{Mo}_2\text{C}$ , which leads to an increase in hardness,

tensile strength, yield and other undoubtedly important Invar properties. [81]. Besides, molybdenum is introduced to reduce preferential allocation of particles of strengthening phases along the grain boundaries, which leads to an increase in toughness.

While simultaneously doping with vanadium and molybdenum the complex carbides (Mo V) C are formed [19]. The maximum amount of molybdenum required for this purpose should be no more than 5%. When the content of molybdenum in the alloy is less than 0.02% its effect on the properties is practically absent. For example, the influence of alloying elements of vanadium and molybdenum on hardness and CTE in invar alloys is analyzed in the article [78]. Complex doping by these elements is most effective for increasing of hardness without increasing the values of the coefficient of linear expansion. When 4.6 % vanadium and 3.8 % molybdenum were added to the base Invar alloy, there was an increase in the hardness by 180 HB, without hardening heat treatments, and the CTE retained the values below  $\alpha = 4.6 \times 10^{-6} K^{-1}$ . With a further increase in the content of vanadium and molybdenum decrease in deformation resistance values is observed. This is due to the increase in the size of carbides.

The effect of the titanium introduction is similar to the introduction of vanadium [60, 68, 82]. It inhibits the growth of grains during heating of the alloys for quenching and thereby prevents embrittlement already at its content of not less than 0.05%. In these studies, it was shown that if the titanium content in the alloy is less than 0.05%, its effect on the grain growth and, consequently, on the mechanical properties is insignificant. Introduction of titanium into carbon containing alloys also promotes the formation of stable titanium carbide and hardening of alloys. However, when the titanium content is greater than 4%, a significant increase in the coefficient of thermal expansion takes place.

Therefore, to increase the titanium content of the alloy greater than 4% is inappropriate [6].

Cobalt is not a carbide-forming element and is introduced primarily to reduce the amount of thermal expansion [11]. This element is found in the FCC lattice of the Fe-Ni alloy by the substitution type, displacing nickel, as it has high affinity with it. Increasing the cobalt content higher than 18-20% increases the temperature of the beginning of the martensitic transformation at which the alloy loses the invar properties [83]. When the cobalt content is less than 2% its effect is almost negligible, because the CTE is not reduced. In the article [84] it is noted that the presence of manganese, chromium, titanium, copper and carbon in the composition of Invar alloys increases the coefficient of linear expansion, in contrast to cobalt, which lowers the expansion coefficient.

### **1.3. Hardening heat treatment of Invar alloys**

A well - known way to improve the mechanical properties of Invar alloys is a deformation processing, however, the deformation cannot be used as a hardening treatment for the articles of a complex geometrical shape [85]. One of the ways to impact on the structural parameters of the mechanical and thermal properties (coefficient of linear expansion) is Invars heat treatment. By changing the parameters of the thermal effects it is possible to increase or, conversely, to reduce the level of mechanical properties and still maintain the minimum value of the CTE in the minimal range and to vary them in accordance with their objectives.

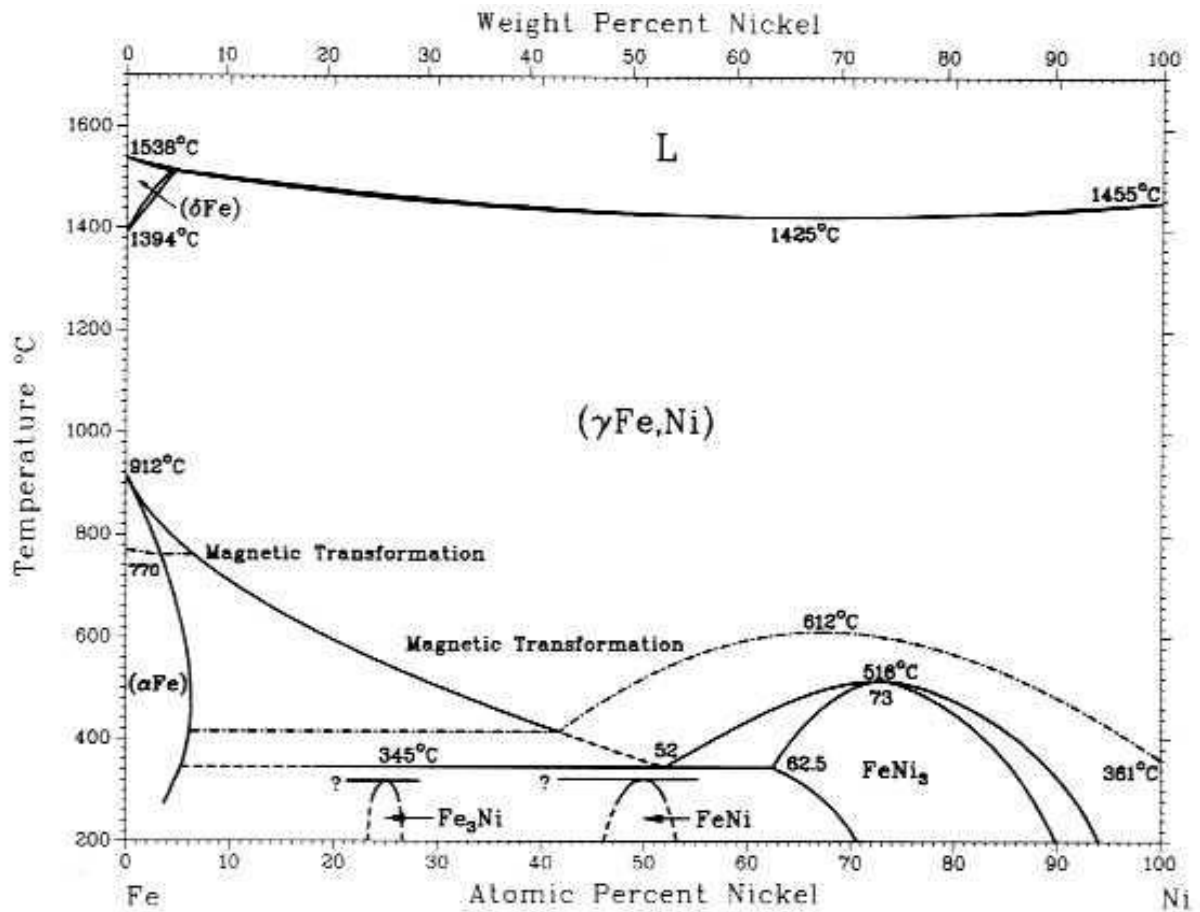
Heat treatment of the traditional invar compositions based on Fe-Ni system usually consists of the quenching and subsequent tempering and special stabilizing processing characteristic only for invar alloys. So the recommended heat treatment for the classic alloy 36H consists in quenching from 830-850 °C

(soaking 30 min.), followed by tempering at 315 °C (soaking 1 hr.) and holding at 95 °C for 48 hours [86].

The initial structure prior to heat treatment of the classic alloy 36H is a homogeneous solid solution consisting of austenite grains [87]. In accordance with the phase equilibrium diagram of Fe-Ni system while heating the classic Invar alloys with a nickel share of about 36% the structure is in the austenitic state with an FCC lattice up to the transition temperature to a liquid state - 1430 °C (Figure 1.5) [88]. Martensitic transformation start temperature for the Invar is in the range of negative temperatures. On this basis, it can be stated that both during heating for quenching, and cooling, the polymorphic transformation does not occur, but hardening is carried out at a supersaturated solid solution.

For non-alloyed invar system Fe-Ni heating for quenching provides a uniform distribution of chemical elements in the austenite and eliminates the defects of the previous deformation processing such as forging or rolling [89]. In addition, homogenization of a solid solution and distribution of nickel uniformly throughout the whole volume prevents forming the areas overly enriched or depleted by it. As it has been mentioned earlier, the formation of such areas has a negative impact on the basic property of Invar alloys that is the CTE increases. During exposure at 830-850 °C the grain does not have time to grow significantly, but with increasing heating temperature for quenching, many researchers have faced the uncontrolled growth of the grain, which has a negative impact on the mechanical properties of the finished product [81, 90]. After quenching, the alloy is a homogeneous solid solution consisting of austenitic grains. Due to a sharp cooling a non-equilibrium structure is formed in the Invar, characterized by higher levels of stress, which allows some increase in mechanical properties [43, 48]. During the work of the finished part in the composition of a unit at higher temperatures the process of softening, the

annihilation of defects and changes in the internal structure of the alloy begins. This significantly changes the expansion coefficient that hinders the use of quenched alloys without subsequent heat treatment. That's what causes the CTE instability while heating the samples with a non-equilibrium structure [85, 91].



**Fig. 1.5** Diagram of phase equilibrium of the system Fe-Ni [88]

When hardening of Invar alloys the researchers use different cooling medium: water, oil, air [47]. However, in the literary sources of data on the effect of quenching media on the structure and properties is evidently not enough.

The non-equilibrium state of the alloy at room temperature is maintained for a long time, since the thermal motion of the atoms is not enough. Heating of metal, which is a result of the previous processing received an unstable state, allows to transfer the Invar alloy with a non-equilibrium structure in a state of equilibrium [83]. Typically, classical invar alloys are subjected to annealing in the temperature range 350-500 ° C for 1-3 hours [2, 4, 12, 43]. Heating to these temperatures increases the thermal mobility of atoms and accelerates the processes (stress relief, reducing the distortion of the crystal lattice, diffusion), leading a metal in a more stable state [2, 4, 31].

Along with a low coefficient of thermal expansion of one of the most important characteristics of Invar alloys is a thermal and temporal stability of size. A gradual increase in coefficient of linear expansion and the change in length over time by natural aging, even at room temperature is characteristic for invar alloys [93]. As a result, the sizes of products made of Invars at prolonged lifespan or storing completely at rest at a constant temperature change significantly [94]. Metrological surveillance conducted over the years, revealed that samples of Invars tend to lengthen over time. The most significant changes occur in the first years, then there comes a time of a stable state. Duration of the period until stabilization is from 15 to 40 years. It should be noted that the change in length of the individual sections of the samples is not the same, which can be explained by the presence of enriched and depleted nickel sites [95]. To improve the temporal stability of the system Fe-Ni of the Invar alloy samples the thermal treatment is used, which is called stabilizing. It consists in the exposure of the samples at 95 °C for 48 hours. It is this mode that allows minimizing the increase in the absolute size of samples or finished products for use in various temperature conditions [96, 97].

Modern high-tech industries using the Invar alloys for the manufacture of critical parts and mechanisms, put new demands arising from the need to

improve mechanical properties while maintaining low CTE values. The Invar alloys of traditional chemical compositions, even after hardening heat treatments are not able to provide the necessary level of mechanical properties, making them difficult to use.

Increase of strength characteristics in Invar alloys is possible in various ways. So in the research of A.I. Uvarov, V.V. Sagaradze et al. it is shown that the hardening of the alloy system Fe-Ni-Co-Ti was provided by isolation of intermetallic phases while aging [98, 99], but the values of CTE remained high. Since the beginning of the 80's a number of domestic and foreign scholars have created and investigated the alloys in which hardening was created, thanks to the allocation of persistent carbides of the alloying elements such as tungsten, titanium, molybdenum, vanadium, and others. However, the carbon introduction for creating chemical compounds with the listed elements exerts an extremely negative impact on the value of the coefficient of expansion, increasing it. The result of these studies became high-strength Invar alloys with a coefficient of expansion in the range of  $4 \times 10^{-6} K^{-1} \leq \alpha \leq 7 \times 10^{-6} K^{-1}$ . These values of CTE do not correspond to the term a low coefficient of linear expansion [2] and the use of such alloys in the precision engineering is difficult. In recent years new types of high-Invar alloys with minimum values of CTE based on the system Fe-Ni-C and Fe-Ni-C-Co with additional alloying carbide-forming elements have been created, which together with high strength properties are different from global analogues by a low coefficient of linear expansion [100, 101]. Heat treatment of Invar alloys of the Fe-Ni-C system and its impact on the structure and properties was investigated in the researches of J.L. Rodionov et al [6, 16, 22-25], A.S. Zilin [70], A.A. Braid [17], A. Nakama [18] and others, both domestic and foreign scientists.

Typically, heat treatment of high strength invar alloys of the above mentioned systems consists in quenching from 1000-1300 °C with holding time and various cooling media, followed by aging at temperatures ranging from 300 to 800 °C with soaking from 30 minutes to 10 hours. The temperature-time regimes depend on many factors, including the chemical composition, the initial state before the heat treatment and the predetermined level of mechanical and thermal properties, as well as parameters of the structure [15, 17, 34, 63, 68, 69, 71].

The heating temperature for hardening and the holding time at this temperature should ensure dissolution of the largest possible proportion of the carbide phase and thus prevent grain growth. However, in the study [81], researchers have found that while heating at temperatures above 1200 °C the hardness begins to decrease, due to uncontrolled grain growth, while even at such high temperatures it is impossible to completely dissolve all carbide particles [20]. After hardening Fe-Ni-C Invars doped by carbide-forming elements become supersaturated solid solutions capable of decay. Binding energy of atoms in the crystal lattice at room temperature is sufficient to ensure the conditions of atoms movement, i.e., natural aging is possible, resulting in the change of expansion coefficient of hardened alloys with time. Therefore, the use of hardened Invars, as noted above, is difficult.

If in classical invar alloys heating after quenching is used to remove quenching stresses in the high doped Invars it is necessary for the flow of the aging process and of implementation of mechanisms of precipitation hardening to release the carbide phase from the saturated solid solution. According to the literature data [102] the active movement of atoms in the face-centered crystal lattice of the austenite begins at 300-350 °C. This means that below this temperature, the movement of atoms will occur not as active, and a large amount of time will be required to reach equilibrium. To speed up the process of separation of



dispersed particles from a supersaturated solid solution it is necessary to raise the aging temperature above 300-350 °C [103].

The results of studies of the heat treatment effect on mechanical properties of the Invar Fe-Ni-C-Co-V alloy are given in the article of O.M. Ogorodnikova and E.V. Maximova [77]. The researchers managed to achieve the increase of hardness and strength by about 30% compared with the tempered condition having used annealing. The mode by which these results were obtained is quenching at 1100-1200 °C followed by annealing at 700-800 °C.

#### **1.4. Setting goals and objectives of the study**

In the works of many local researchers, such as A.I. Uvarov, O.M. Ogorodnikov, S.V. Grachev, V.A. Zakharova, V.V. Sagaradze, J.L. Rodionov, et al., as well as foreign scientists Zhang Jian-Fu, Tao Wen, K. Nakama, K. Sugita, J.B. Darby, C. Giolli, M. Turbil et al., the features of formation of the structure and properties of Invar alloys of different chemical compositions are described. Analytical review showed that the classical Invars, which are used for the manufacture of products in the aerospace industry, laser parts, measurement and metrological equipment, do not have the necessary strength properties even after hardening treatments. Meanwhile, modern high-tech industrial sectors are in need of Invar alloys with improved strength characteristics.

Recently, new high-strength invar alloys with minimum values of CTE based on the Fe-Ni system with the introduction of carbon, cobalt and carbide and the forming alloying elements that provide strengthening by allocating of carbide phases have been created. Research aimed at the development of industrial technologies of blanks production from these innovative high-strength Invar alloys has been conducted by the scientists of the " Nosov Magnitogorsk State

Technical University" in cooperation with the specialists of "Motovilikhinskiy plants" for several years. In accordance with the specifications the ultimate strength of alloys must be at least  $800 \text{ N / mm}^2$  and the coefficient of linear expansion in a temperature range from 20 to 150 °C should be between 0.5 and  $3 \times 10^{-6} \text{ K}^{-1}$ .

However, there is still no consensus on the laws governing the formation of the structure, mechanical and thermal properties by heat treatment of Invar alloys class of the system Fe-Ni-CV, Fe-Ni-C-Co-V and Fe-Ni-C-Mo with a minimum value of CTE.

And there is currently no single, accepted by the scientific community opinion on the changes of the structure and properties during heat treatment of Invar alloys class of the system Fe-Ni-C-V, Fe-Ni-C-Co-V and Fe-Ni-C-Mo with a minimum value of the coefficient of linear expansion. There are no strict dependency values of hardness, strength, coefficient of linear thermal expansion from the mode of heat treatment of the alloys of these systems.

Until recently, the literature contains only a few uncoordinated data on the effect of heat treatment on the value of coefficient of linear expansion and mechanical properties of high - strength Invar alloys with a low coefficient of thermal expansion. Therefore, the study of the features of structural changes course during heat treatment and their influence on the properties of Invar alloys that provide improved performance characteristics, satisfying the needs of knowledge-intensive industries in advanced materials for special purposes, is an urgent task.

The relevance of the work is also supported by its compliance with the topics of the integrated project to create a high-tech production, conducted with the participation of the Russian higher educational institution (contract № 02.G25.31.0040), as well as with the tasks implemented within the framework

of their officially recognized in RF Technology Platform " Metallurgy and new materials technology (i. 21 Materials and metallurgy technologies)."

**The objective of the research** is the definition of heat treatment regimes for improving the strength values while maintaining a low coefficient of linear expansion of Invar alloys, Fe-Ni-C system, alloyed with cobalt, vanadium and molybdenum.

To achieve this goal the following main objectives were set and solved:

1. To investigate the impact regularities of time-temperature regimes of pre-heating for quenching and of the cooling fluid on the structural characteristics and mechanical properties of Invar alloys of the Fe-Ni-C system, additionally alloyed with cobalt, molybdenum and vanadium.
2. To identify the effect of heat treatment regimes while heating of the hardened Invar alloys on their structure and mechanical properties.
3. To set the behavior of the temperature coefficient of linear expansion, in high- strength Invar alloys under thermal exposure.
4. To propose recommendations for heat treatment regimes of invar alloys to provide increased levels of strength ( $UTS \geq 800 \text{ H/MM}^2$ , the hardness of 250-400 HV) and maintaining the thermal expansion coefficient in the low range ( $\alpha \leq 3 \times 10^{-6} \text{ K}^{-1}$ ).

# CHAPTER 2

## MATERIAL AND METHODS OF RESEARCH

### 2.10 Research materials and methods of treatment

For the study were selected Fe-Ni-C invar alloys system, alloyed with cobalt, vanadium and molybdenum at various concentrations. Alloy grade and chemical compositions shown in Table 2.1. When selecting materials for the study came from the technical requirements imposed "Motovilikhinskiy plants", and analysis of information and patent literature [23-25].

**Table 2.1** Alloy grade and chemical compositions

Alloy grade	Mass concentration of elements, %										
	Ni	C	V	Mo	Co	Si	Mn	P	S	Ti	Al
32NF	32.5	0.76	1.7	0.01	0.05	0.14	0.17	0.006	0.001	0.086	0.039
34NFM	34.7	0.40	1.40	2.30	0.04	0.12	0.22	0.005	0.001	0.090	0.018
32NFK	33.0	0.40	1.46	0.01	4.70	0.08	0.19	0.005	0.001	0.160	0.059

The alloys were melted in a vacuum induction furnace at 60 kg ingots with various deoxidation variants that have been selected based on an analysis of literary sources [104-108]:

1. 0.1 % Al, 0.2 % Si and 0.1 % Mn;
2. 0.2 % Mn and 0.5 % Ti;
3. 0.2 % Si, 0.2 % Mn and 0.2 % SiCa;
4. 0.1 % Al, 0.2 % Si, 0.1 % Mn and 0.35 % NiMg(0.15%Mg);

5. 0.15 % Mn<sub>ruf</sub>, 0.35 % NiMg(0.15%Mg), 0.1 % Si<sub>cr</sub>, 0.1 % SiCa, 0.06 % Al and 0.07÷0.1 % Ti<sub>sponge</sub>;

Smelted ingots were forged to a diameter of 50-70 mm, and subjected to hot rolling to the required size of the final the cross section 12 mm.

Hot rolled billets were subjected to the following heat treatment:

- Quenching from a temperature of 1200 or 1250 °C with cooling in water and oil;
- Aging prequenched samples at 300, 500, 600, 650, 700 and 800 °C, soaking for 1 hour and cooling in air;
- Heating and maintenance of the samples at 80 °C for 48 hours.

Heat treatment was carried out in a laboratory electric furnaces PL 20 and PL 5, the maximum working temperature is 1250 °C. Quenching was carried out the transfer of the sample in the quenching medium. Transfer time is less than 1 second.

## **2.11 Methods of physical modeling of heat treatment**

Physical modeling of heat treatment study Invar alloys was carried out on samples of 10 mm and 80-90 mm in diameter and was carried out at the research complex Gleeble 3500. A special feature of the complex is the ability to maintain a homogeneous temperature in the center of the cross-sections of the sample at different heating or cooling modes.

Heating the samples is carried out by electrical warming, which allows to realize any heating rate and maintain a constant temperature. Due to the high thermal conductivity of grips that hold the sample, and special tools «ISO Quench», is possible to achieve high cooling rates up to 1000 °C/sec, which is allowed to implement the physical modeling of quenching [109-115].

Heating of the samples to for quenching temperature 1200 and 1250 °C was performed at 2 °C/sec. Homogenization soaking at these temperatures was 15 minutes long. The cooling rate simulating quenching in water, was 250-300 °C/sec. The heating of the sample to the temperature of aging was carried out at a rate of 1 °C/sec.

The experiment was controlled by QuikSim2®, software that allows you to set each of the actions in the modeling process, the order and duration (Figure 2.1).

#	L	Time	Axis 1	Axis 2	Axis 3	Comment	
1			System	Setup	Limits: Compression=-150mm, Force=50000kgf, Heat=100% [table.gin]		
2			Stress/Strain	Axial strain using Stroke, l = 12.00mm, d = 10.00mm			
3			Acquire	Dilatometer	Dilatometer.line	Force Force.line PowAngle PTemp TC1	
4			*				
5			*				
6			*				
7			Start	<input checked="" type="checkbox"/> Mechanical	<input type="checkbox"/> High	<input checked="" type="checkbox"/> Thermal	
8			Mode	Force(kN)	Torsion(rev)	TC1(C)	
9			Zero	Dilatometer			
10			Sample	100,0Hz			
11			GSL>	set TC1KP to 0.7			
12			GSL>	set TC1KI to 0.7			
13		00:10,0000		0,0	0	30	
14		10:00,0000		0,0	0	1250	
15		15:00,0000		0,0	0	1250	
16			Switch	Quench3	<input checked="" type="checkbox"/> On		
17			Switch	Quench4	<input checked="" type="checkbox"/> On		
18		00:00,1000		0,0	0	1250	
19		00:01,0000		0,0	0	100	
20			GSL>	wait TC1<100C			
21			Switch	Quench3	<input type="checkbox"/> Off		
22			Switch	Quench4	<input type="checkbox"/> Off		
23			End	<input type="checkbox"/> Mechanical	<input type="checkbox"/> High	<input type="checkbox"/> Thermal	

**Fig. 2.1** Window of experimental program in QuikSim2

The data were analyzed using the software package Origin® that has mathematical functions for data analysis and provides quick and easy analysis of each test.

## 2.12 Methods dilatometric analysis and determination of the coefficient of linear expansion

Dilatometric investigations were also carried out using a complex Gleeble 3500, in packaging arrangement which includes a high-precision dilatometer. The dilatometer sensor operates on the principle of LVDT (linear differential transformer). Dilatometer resolution is 0.4  $\mu\text{m}$  and allows to implement assigned tasks, especially when abnormal low values of coefficient of linear expansion. The samples had a diameter of 10 mm and a length of 80-90 mm, necessary for their fixation in the grips of the complex Gleeble 3500 heating system [110]. In the middle of the length of the sample by spot welding was attached chromel-alumel thermocouple for temperature control test.

Complex functions are adapted to determine the coefficient of linear expansion [111-113], which carried out in accordance with the procedure described in standard GOST 14080-78 [43]. Thermal tests corresponded to Appendix № 4 of standard and consisted of heating to 150  $^{\circ}\text{C}$  with a rate of 150  $^{\circ}\text{C}/\text{hour}$ , soaking at this temperature for 20 minutes and cooling the sample to room temperature. The results of dilatometric tests presented in the form of a graph of the change in the linear size (diameter) of the time, which determines the coefficient of linear expansion. The value  $\Delta L$  (change of diameter) to calculate coefficient is taken in the last point of isothermal soaking.

CTE in a given temperature range was calculated by the formula:

$$\alpha_{20-T} = \frac{\Delta L}{L \times \Delta T} ,$$

where  $\Delta L$  - change the sample diameter, mm;

L - start diameter of sample, mm;

$\Delta T$  - temperature difference in the test,  $^{\circ}\text{C}$ :

$$\Delta T = T - T_{start.},$$

where T - the upper value of temperature range determination coefficient of linear expansion, °C;

$T_{start.} = 20$  ° C - the temperature in the beginning of the test.

### **2.13 Method of light microscopic analysis**

For the metallographic analysis were prepared metallographic section. The samples were cut by means a precision cutting machine Buhler IsoMET 4000 and were pressed at 1000 Simplimet automatic press in resin «Transoptic». Blanks were subjected to abrasive grinding on different grain sizes on grinding and polishing machines line sample preparation Buechler. Samples before changing the skin be carefully rinsed in a jet of water to remove particles of abrasive powder. After grinding on grinding skins samples were polished using diamond paste and diamond suspensions of varying granularity. To identify the microstructure of thin surface subjected to etching in the reagent composition HNO<sub>3</sub> (65-68% wt.) and HCl (32-35% wt.) in the ratio 1: 3 by volume, of the polished surface by dipping into a bath of the reagent.

Studies of the microstructure was performed on Meiji Techno optical microscope in bright field at magnifications of 50 to 1000 with the use computer image analysis system Thixomet PRO.

### **2.5 Method of scanning electron microscopy and electron probe micro analyzer**

Scanning electron microscopy (SEM) analysis was performed using a scanning electron microscope JSM-6490 JEOL LV at an accelerating voltage of 30 kV.



Research was carried out on microsections used for light microscopy, in the modes of secondary and backscattered electrons at magnifications up to 50.000 times.

Electron probe micro analyzer was also performed on the microscope JEOL JSM-6490 LV with a special system of energy dispersive spectral analysis INCA Energy 450.

## **2.6 Method of quantitative analysis**

Determination of the grain size was performed on an optical microscope Meiji Techno with the use computer image analysis system Thixomet PRO. The image of the microstructure using a digital camera is inserted into the computer and then analyzed with the use of specialized programs that are adapted to the Standard [22].

Determination of the particle size of the second phase was carried out in Thixomet PRO software environment adapted to work with the SEM images. Sample volume ranged from 150 to 300 units. Relative measurement error does not exceed 5-7%. From the data obtained were constructed curves of density frequency distribution of particle size in which the parameters of distribution were defined. The average value of particle size as the average of all of the numerical values.

## **2.7 Methods of X-ray analysis**

X-ray diffraction analysis was performed on the X-ray diffractometer Shimadzu XRD-7000 X-ray tube with a chromium anode ( $\lambda = 2.285 \text{ \AA}$ ) at a voltage of 40 kV and a current of 30 mA. Continuous shooting was carried out with focus on the Bragg-Brentano in the range of angles  $2\theta$  of 40 to 140 ° at a

rate of 2 °/min. For the absorption of X-rays used K $\beta$  vanadium selective filter. Determination of qualitative phase composition was carried out in a software package International Centre for Diffraction Data PDF-2 Release 2014 with database integrated into it.

## **2.8 Hardness Measurement Technique**

Hardness was determined according to Standard [34] of the universal hardness tester Test M4S075G3 Emso indentation diamond pyramid with an angle between the opposite faces of 136 ° under a load of 3 kg load and 15 seconds duration. As a result of tests on the sample surface to give a print-out in the form of a rhombus, which is automatically measured for both diagonal and made computer processing of the results.

## **2.9 Method for determining mechanical properties in tensile tests**

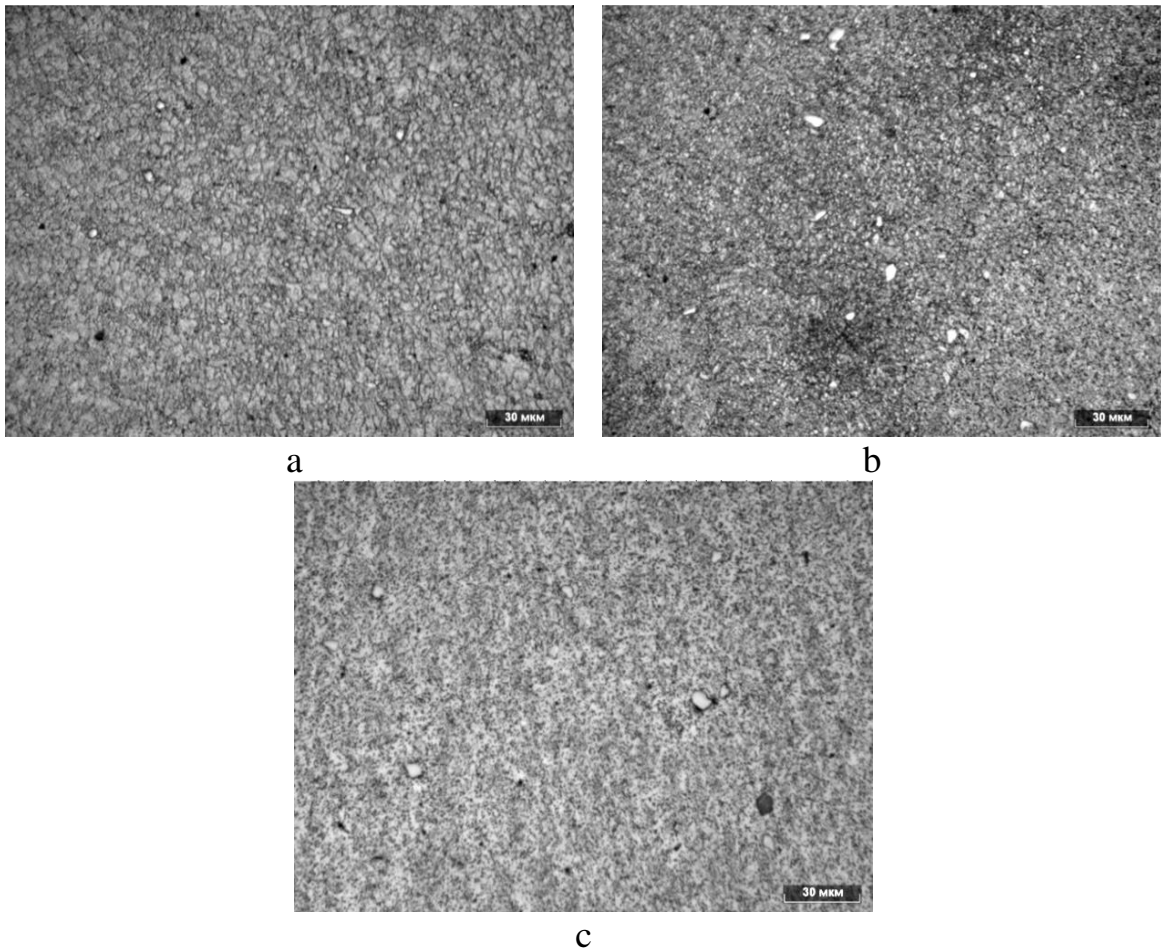
To evaluate the parameters of ultimate tensile strength was applied uniaxial tensile test. For tests using standard samples with a diameter 5.93 mm with an initial estimated working length  $l_0 = 30 \pm 0.5$  mm, with an accuracy limited to 1% of the marks. The samples were made of rods by lathe machining. Tensile tests were carried out in accordance with GOST 1497-84 [12] at a temperature of 20 °C on a Shimadzu machine at a speed of 0.5 mm/min, with diagrams recording and fixing the tension and the current maximum tensile force with accuracy fixed 1 N. Moving fixed after 0.1 s with an accuracy of 0.01 mm. The test results were calculated as the average of five tests.

# CHAPTER 3

## STRUCTURE AND MECHANICAL PROPERTIES OF INVAR ALLOYS IN HOT-ROLLED AND HARDENED STATES

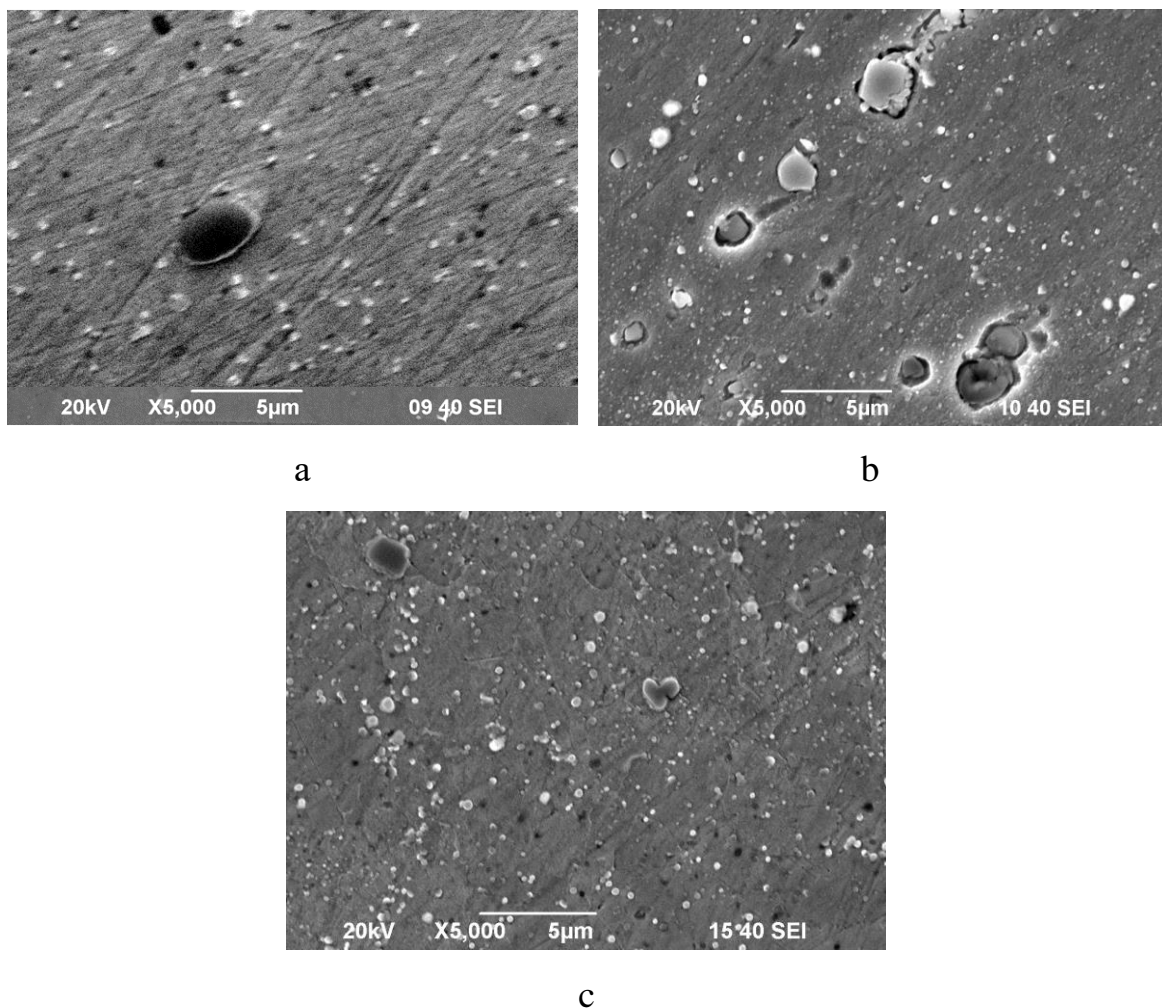
### 3.1 The metallographic analysis results of the Invar alloys structure in the hot rolled state and their discussion

General view of the alloys microstructure being hot rolled in the initial state before heat treatment is shown in Figure 3.1.



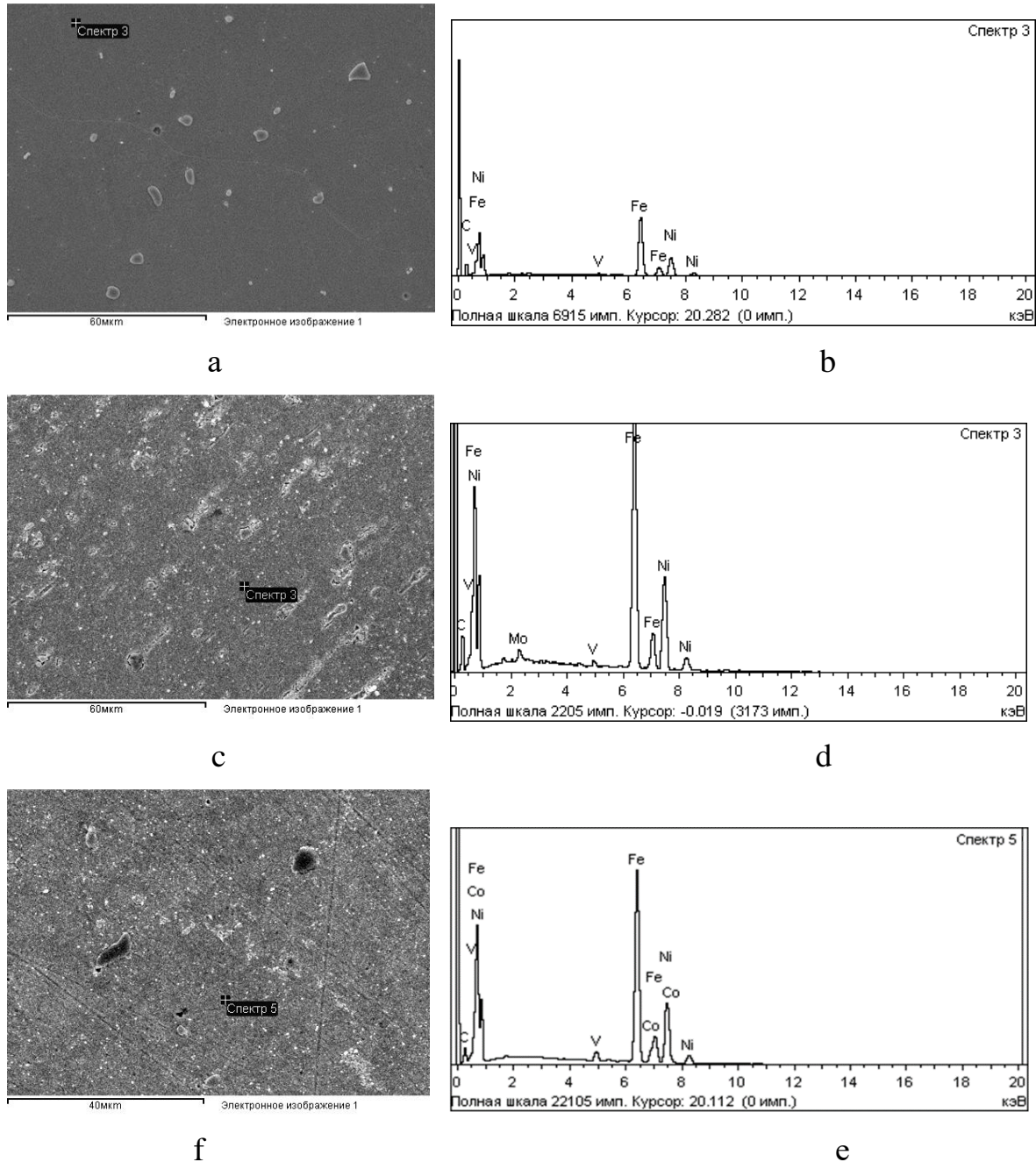
**Fig. 3.1** Microstructure of alloys 32NF (a), 34NFM (b) and 32NFK (c) in the initial state before heat treatment, x 500

The results of the microscopic analysis performed by SEM showed that the microstructure of the alloys is a heterogeneous system consisting of grains of the metal substructure, dispersed and large particles of the second phase (Figure 3.2). The greatest number of particles is found in 32NF alloy with a higher carbon content as compared with alloys 34NFM and 32NFK and a higher content of vanadium in comparison with the alloy 32NFK. The microstructure of the alloys was investigated at high magnifications by SEM (Figure 3.2).

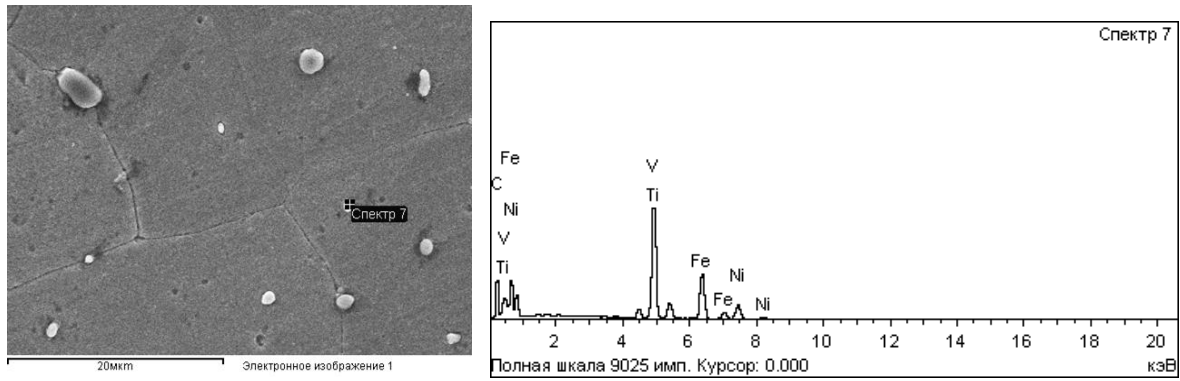


**Fig. 3.2** The second phase particles in the alloy microstructure 32NF (a), 34NFM (b) 32NFK and (c) in the initial state

To identify the chemical elements that make up the structural components of alloys, the electron microprobe analysis was conducted, the results of which are illustrated in figures 3.3-3.5.

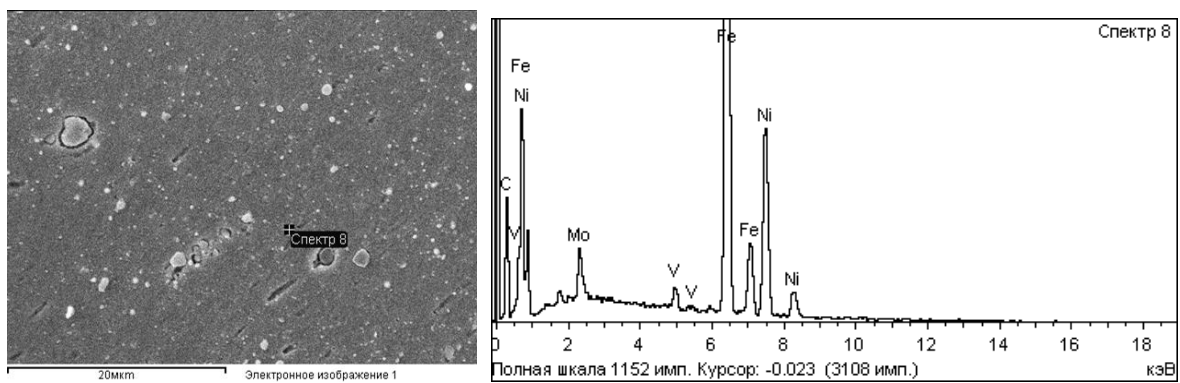


**Fig. 3.3** The electronic image of the investigated areas 32NF alloy microstructure (a), 34NFM (c) and 32NFK (e) in the initial state and the characteristic spectra taken from the matrix (b, d, f)



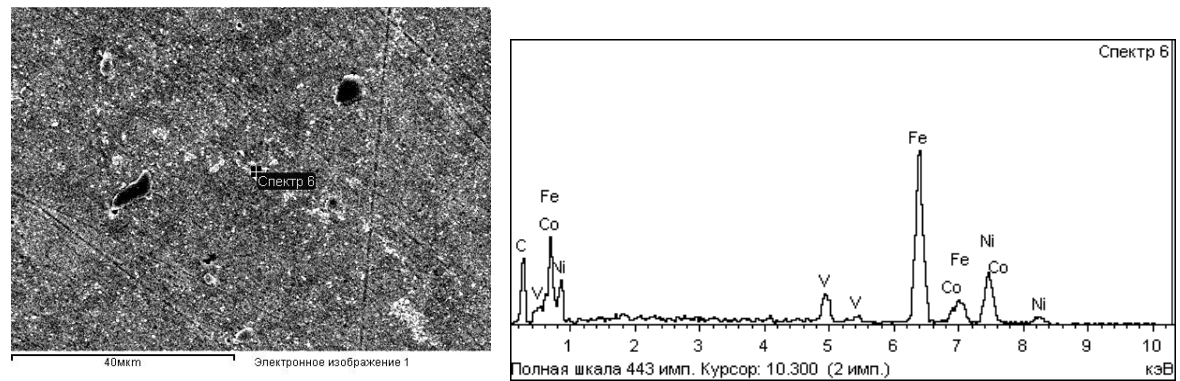
a

b



c

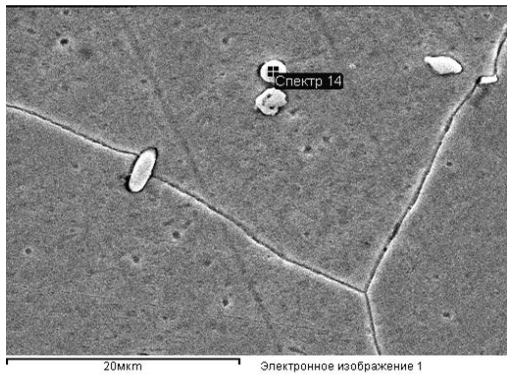
d



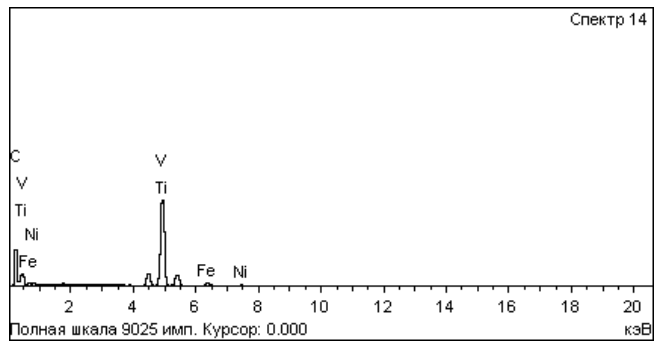
e

f

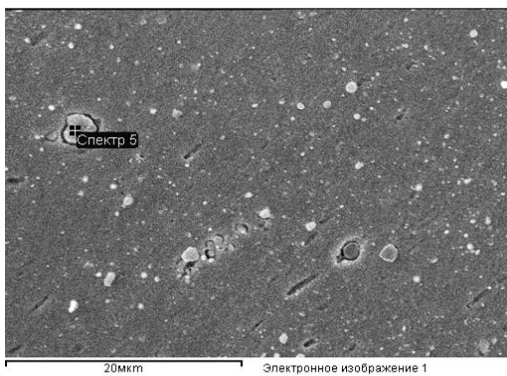
**Fig. 3.4** Electronic image of the investigated areas of the alloys microstructure 32NF (a), 34NFM (c) and 32NFK (e) in the initial state and the characteristic spectra recorded from dispersed particles (b, d, f)



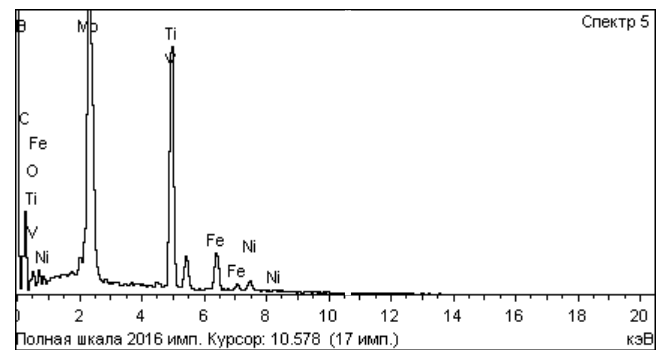
a



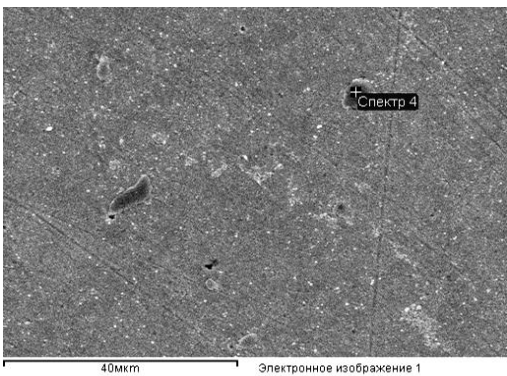
b



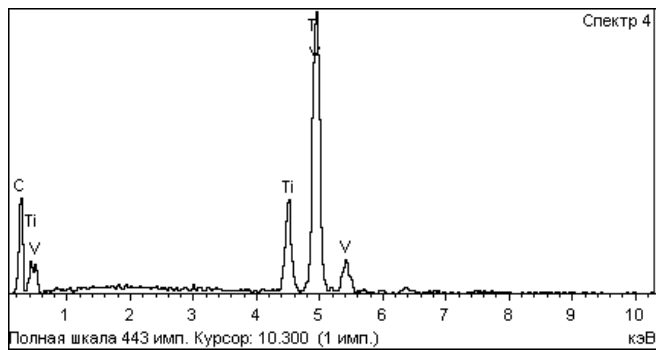
c



d



e



f

**Fig. 3.5** Electronic image of the investigated areas of the alloy microstructure 32NF (a), 34NFM (c) and 32NFK (e) in the initial state and the characteristic spectra taken from the large particles (b, d, f)

In the spectra obtained from the metal base (matrix) of the sample structure, the peaks of iron, nickel and carbon are detected in all the alloys. Besides them in the alloy 32NFK the peaks of cobalt, in the alloy 34NFM the peaks of molybdenum, and in the alloys 32NF, 32NFK and 34NFM the peaks of vanadium are detected (see Figure 3.3.). This allows identifying the matrix of alloys as a solid solution containing these elements. In alloys on the basis of the system Fe-Ni and Fe-Ni- C the authors of the works [2, 19, 21, 42] such a solid solution is identified as gamma-solid solution with face-centered cubic lattice. Deciphering the diffraction patterns obtained by X-ray diffraction confirmed that in the original hot rolled state the metal substrate in all the investigated alloys has the FCC lattice (appendix 1-3), the parameters of which calculated from the results of X-ray diffraction, are given in appendix 4.

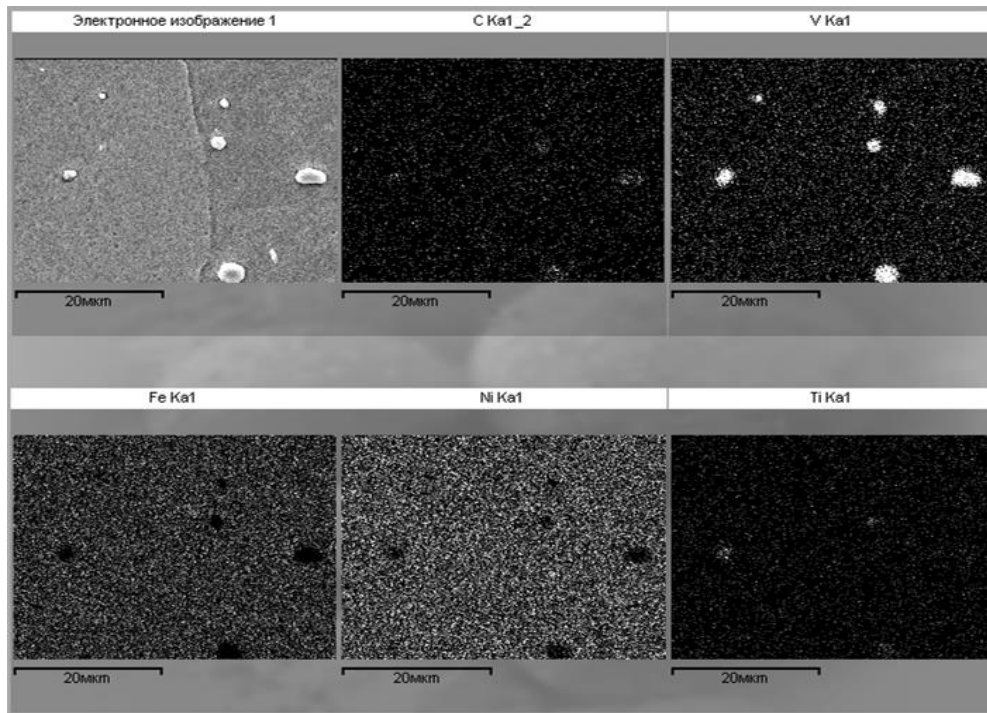
The method of the X-ray diffraction has shown that in the spectra taken from dispersed inclusions, carbon peaks and carbide-forming elements: vanadium in alloys 32NF (as shown in Figure 3.4, b), 34NFM (see Figure 3.4, d.) and 32NFK (see Figure 3.4, f. ) and molybdenum in the alloy 34NFM are present. In some cases, titanium is also found in the dispersed particles (see. Figure 3.4, b).

In the spectra from large particles in addition to carbon the peaks carbide-forming elements are detected: in alloys 32NFK and 32NF vanadium is found (see Figure 3.5, b, f.), in the alloy 34NFM vanadium and molybdenum are detected (see Figure 3.5, d). In the spectra obtained from some of the larger particles, there are peaks of titanium, which is contained in large quantities and often in combination with vanadium (see. Figure 3.5, b, d) or molybdenum (see. Figure 3.5, f).

Maps of distribution of chemical elements have confirmed the obtained results: in the fine and coarse particles carbide forming elements vanadium, molybdenum and titanium are concentrated and virtually iron, nickel and cobalt



are not detected (Figure 3.6-3.8). Thus, based on the results of X-ray micrographic analysis, the particles of the second phase observed in the structure of the alloys in hot rolled condition can be identified as carbides of the alloying elements.

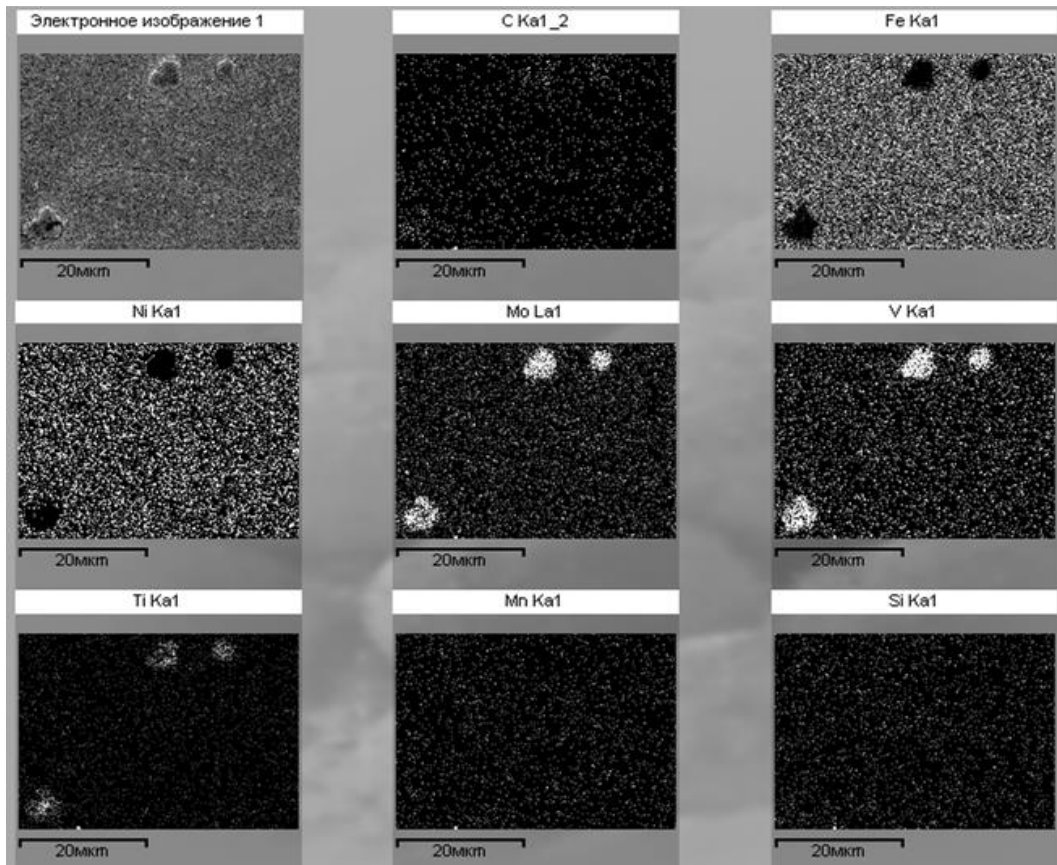


**Fig. 3.6** Electronic image of the alloy microstructure 32NF in the initial state and element distribution patterns

It has been found that in the structure of all the alloys in addition to carbide particles large inclusions are observed in which the electron probe micro analyzer shows the presence of a number of elements specific to non-metallic inclusions of the metallurgical origin. These particles have mainly a rounded shape, which confirms their separation from the melt.

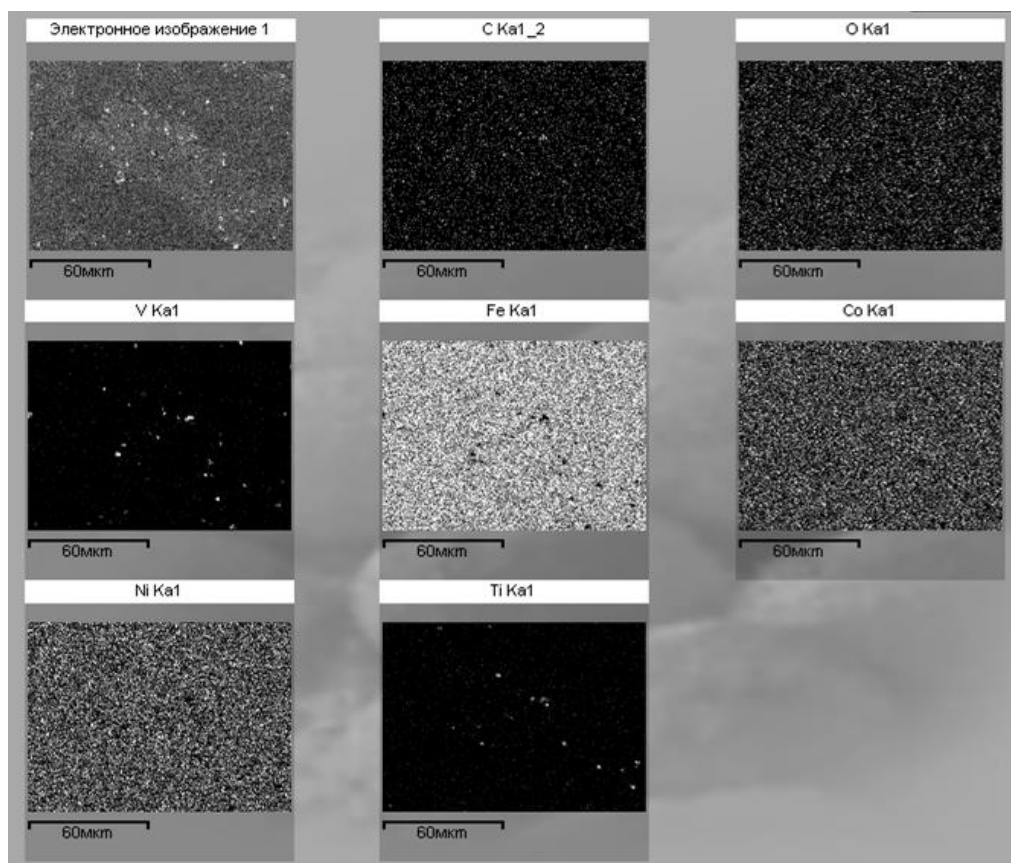
For the alloys based on the system Fe-Ni-C one of the harmful impurities is oxygen which enters the material in the smelting process [109]. It is present in the metal in the dissolved form or in the form of oxide non-metallic inclusions

and deteriorates some of the required final product properties [110-113]. In this regard, great importance have the operation of de-oxidation and the efficient selection of the effective deoxidizer variants, which is essential for achieving the given high values of mechanical properties of the final product.



**Fig. 3.7** Electronic image of the alloy microstructure 34NFM in the initial state and element distribution patterns

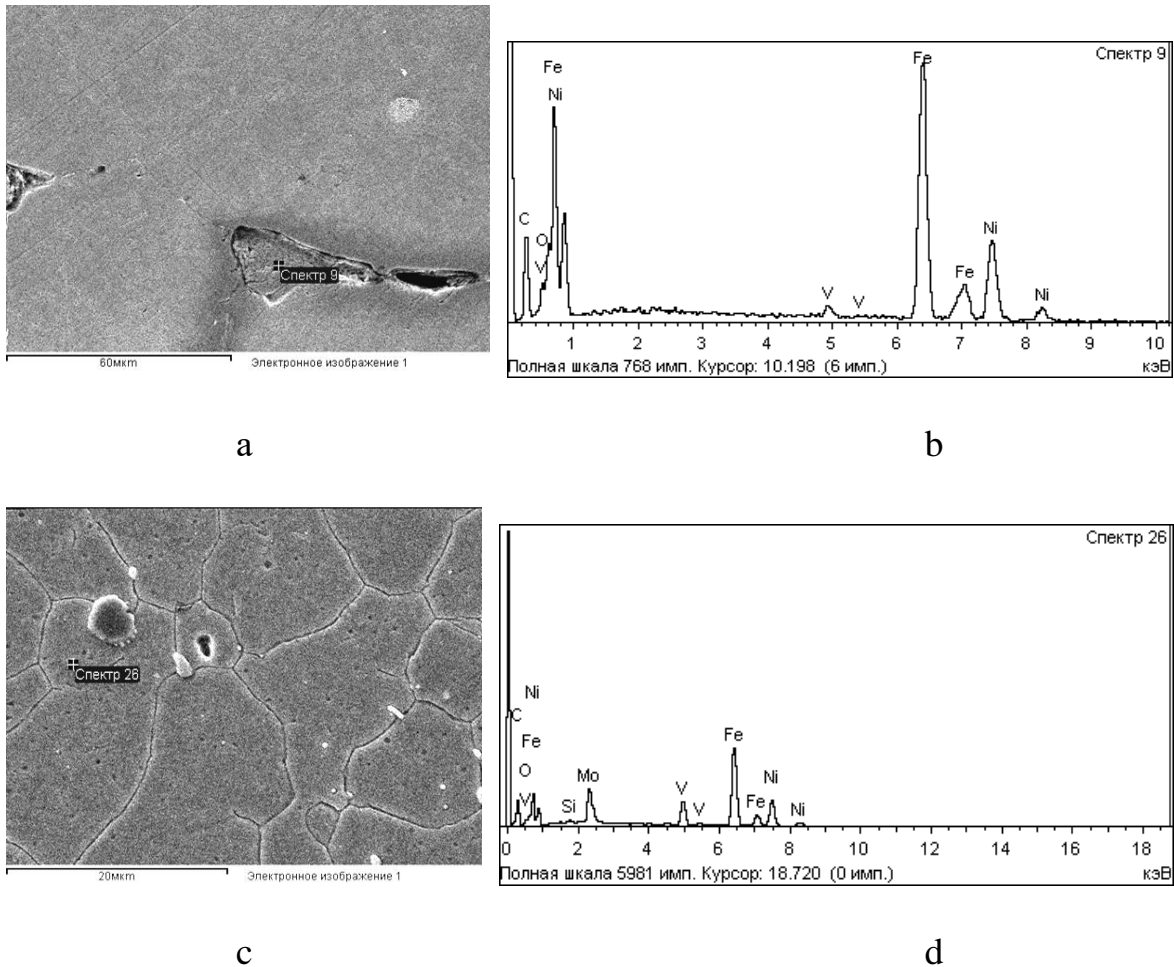
While melting 5 variants of deoxidizing mixtures were used for deoxidation the compositions of which are listed above in Section 2. Therefore, the distribution of elements by the electron probe micro analyzer method in the microstructure and the chemical composition of nonmetallic inclusions in the alloys deoxidized by various compositions were examined [108].



**Fig. 3.8** Electronic image of the alloy microstructure 32NFK in the initial state and element distribution patterns

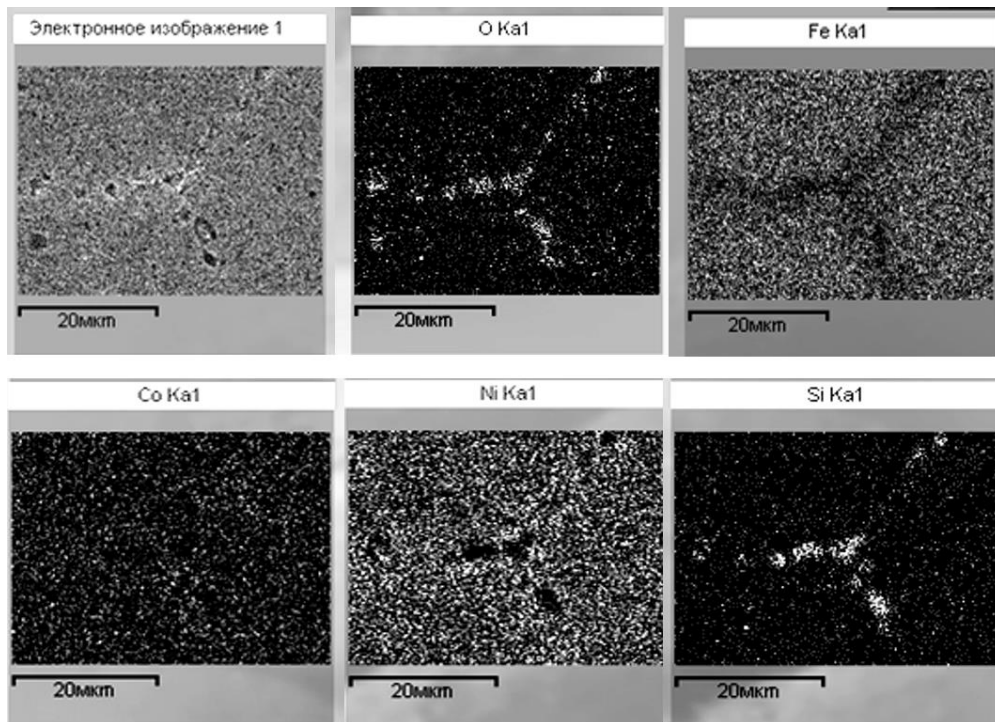
The results showed that in the alloys which had been deoxidized by the deoxidizer of the composition 0.1-0.2% Mn and  $\leq 0.1\%$  Al (variant 1), by the deoxidizer of the composition of 0.2% Si, 0.2% Mn and 0.2% SiCa (variant 3) and by the deoxidizer of the composition 0.1% Al, 0.2% Si, 0.1% Mn and 0.35% NiMg (0.15% Mg) (variant 4), a large number of non-metallic particles impurities was found, in the composition of which oxygen was present (Figure 3.9).

Maps of distribution of the chemical elements indicate that in these particles in addition to oxygen such elements as silicon and aluminum (depending on the composition of the deoxidizer) are present and virtually carbon, iron, nickel, molybdenum, vanadium, cobalt and titanium (figure 3.10, 3.11 ) are absent.

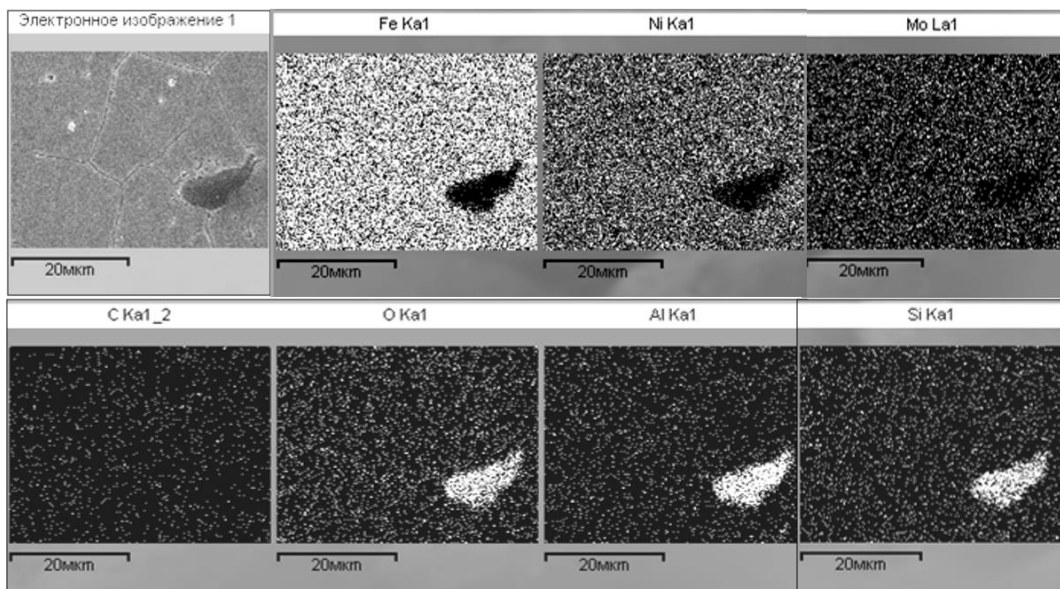


**Fig. 3.9** Electronic image of the researched areas of the microstructure with non-metallic inclusions (a, c) and characteristic spectra taken from the particles in the alloy 32NFK (b) deoxidized according to the variant 1 and in the alloy 34NFM (d), deoxidized according to the variant 3

This indicates that during deoxidation of the Invar alloys by deoxidizers of these compositions (variants 1, 3 and 4) in the investigated alloys there is a large number of oxide non-metallic inclusions having a size of 1 to 60 microns. In some cases, the oxides are arranged in the form of large inclusions and the grid along the boundaries of the grains (Figure 3.10). The findings suggest that less than a complete deoxidation of the investigated alloys while using the deoxidizing compositions of the variants 1, 3 and 4 took place.

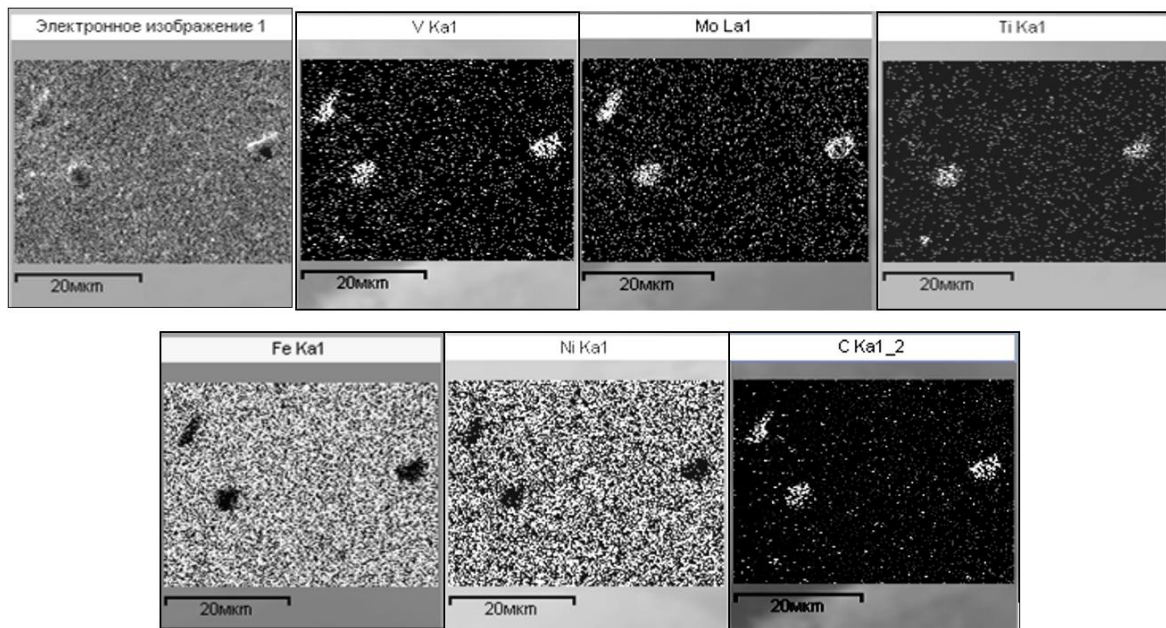


**Fig. 3.10** Electronic image of the grid of nonmetallic inclusions and patterns of distribution of elements in the alloy of the microstructure 32NFK, deoxidized under variant 3



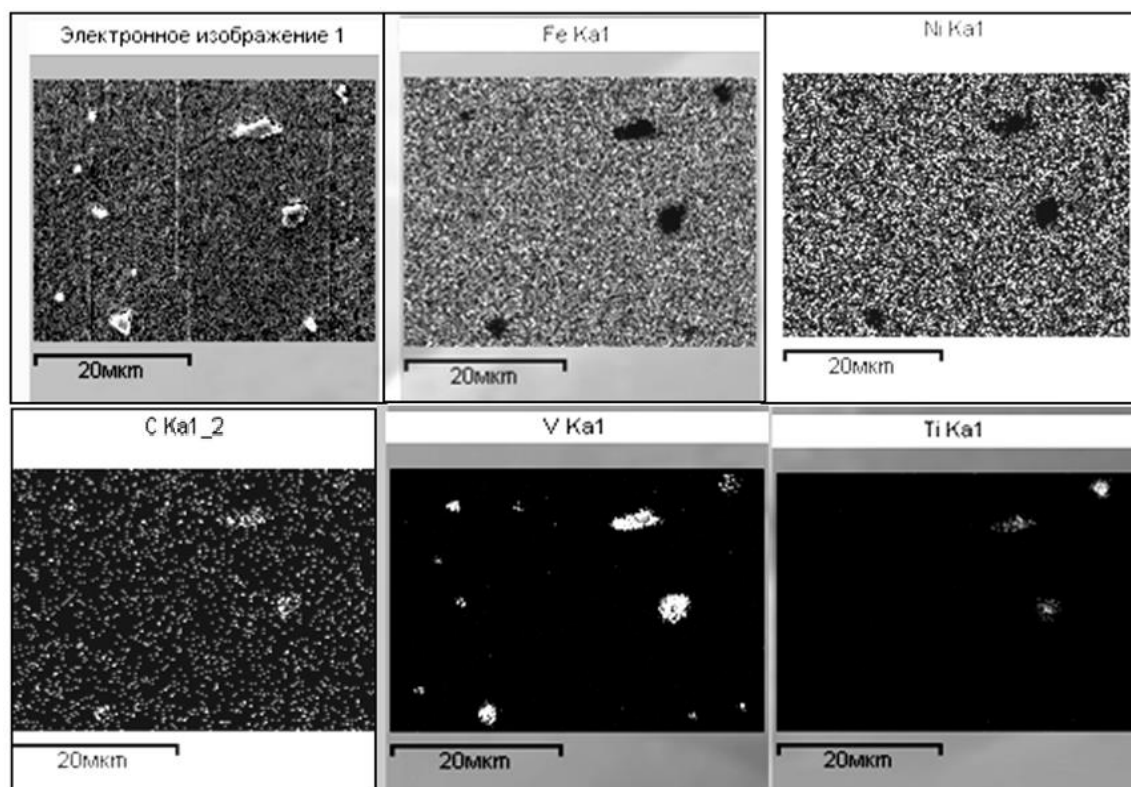
**Fig. 3.11** Electronic image of non-metallic inclusions in the microstructure of the alloy 34NFM, deoxidized under variant 4, and the distribution pattern of elements

When deoxidizing of the alloys with the composition of variant 2 (0.2% Mn and 0.5% Ti), containing a large amount of titanium in the structure there is a large amount of inclusions as small as 2 microns. The presence of titanium is found by the electron microprobe method, and the elements distribution maps indicate that in these inclusions carbon and carbide forming elements - molybdenum and vanadium are also focused and they are present in the alloy composition as alloying additions (Figure 3.12, 3.13). Being the most powerful carbide forming element of the present alloying elements, it forms large carbides in the structure of which vanadium and molybdenum are also included. The alloys deoxidized on the variant 5 ( $Mn_{ref}$  0.15%, 0.35% NiMg (0.15% Mg), 0.1%  $Si_{cr}$ , SiCa 0.1%, 0.06% Al and 0.07 ÷ 0.1  $Ti_{sponge}$ %), non-metallic inclusions of the globular shape are found, in which the structure, as shown by electron microprobe, contains titanium, magnesium, aluminum and oxygen (Figure 3.14). This allows attributing these particles to complex oxides. However, these particles are less in size, in contrast to the particles detected during deoxidation by other compounds.



**Fig. 3.12** Electronic image non-metallic inclusions in the microstructure of the alloy 34NFM, deoxidized under variant 2, and distribution patterns





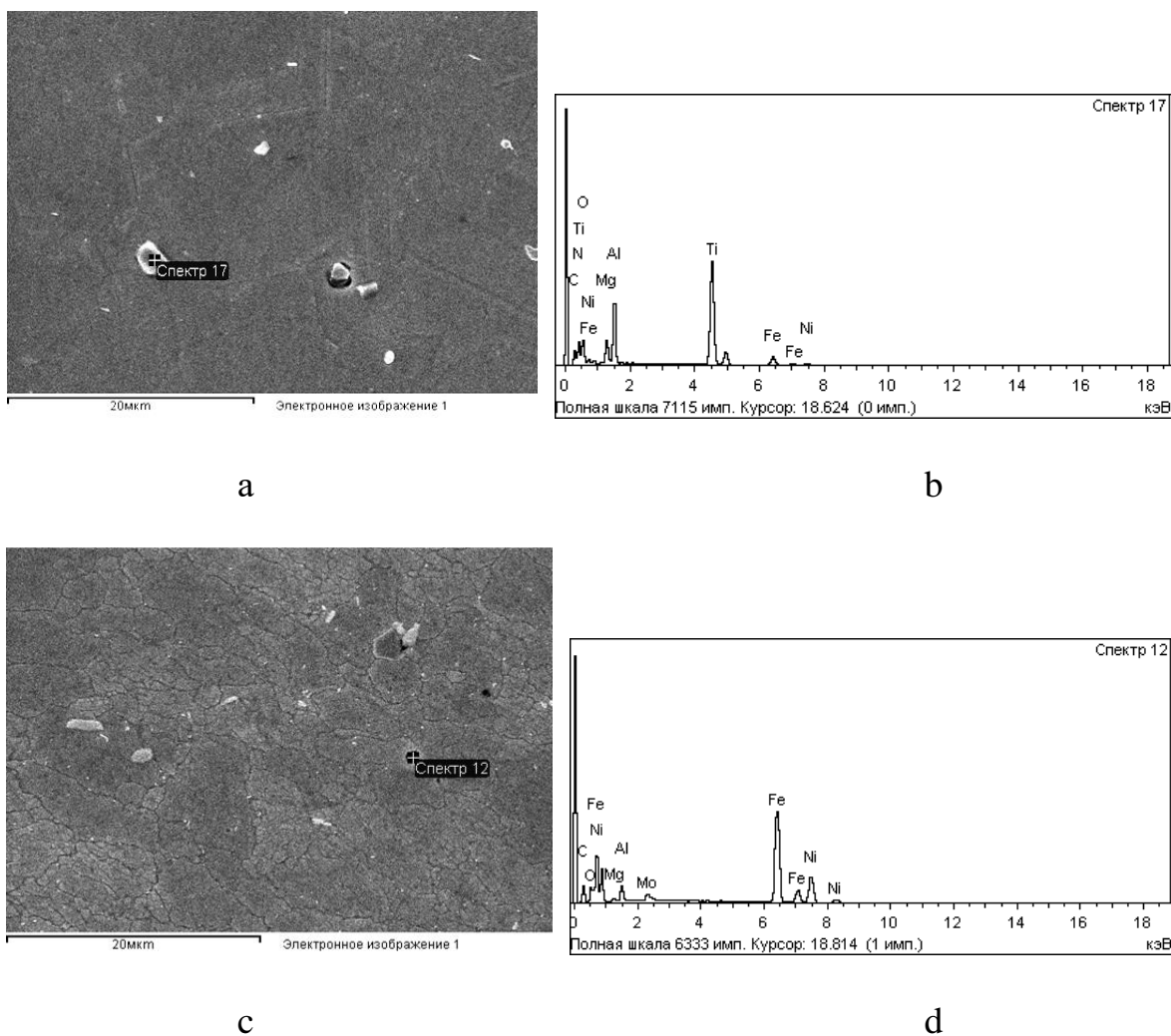
**Fig. 3.13** Electronic image of non-metallic inclusions in the microstructure of the alloy 32NFK, deoxidized under variant 2, and element distribution patterns

### **3.2 The results of metallographic analysis of the hardened structure of Invar alloys under study and their discussion**

The microstructure of the alloys 32NF, 34NFM and 32NFK after quenching from 1200 and 1250 ° C in water is shown in Figure 3.15, and in oil - in Figure 3.16. As before hardening it consists of a metal substructure and particles of the second phase.

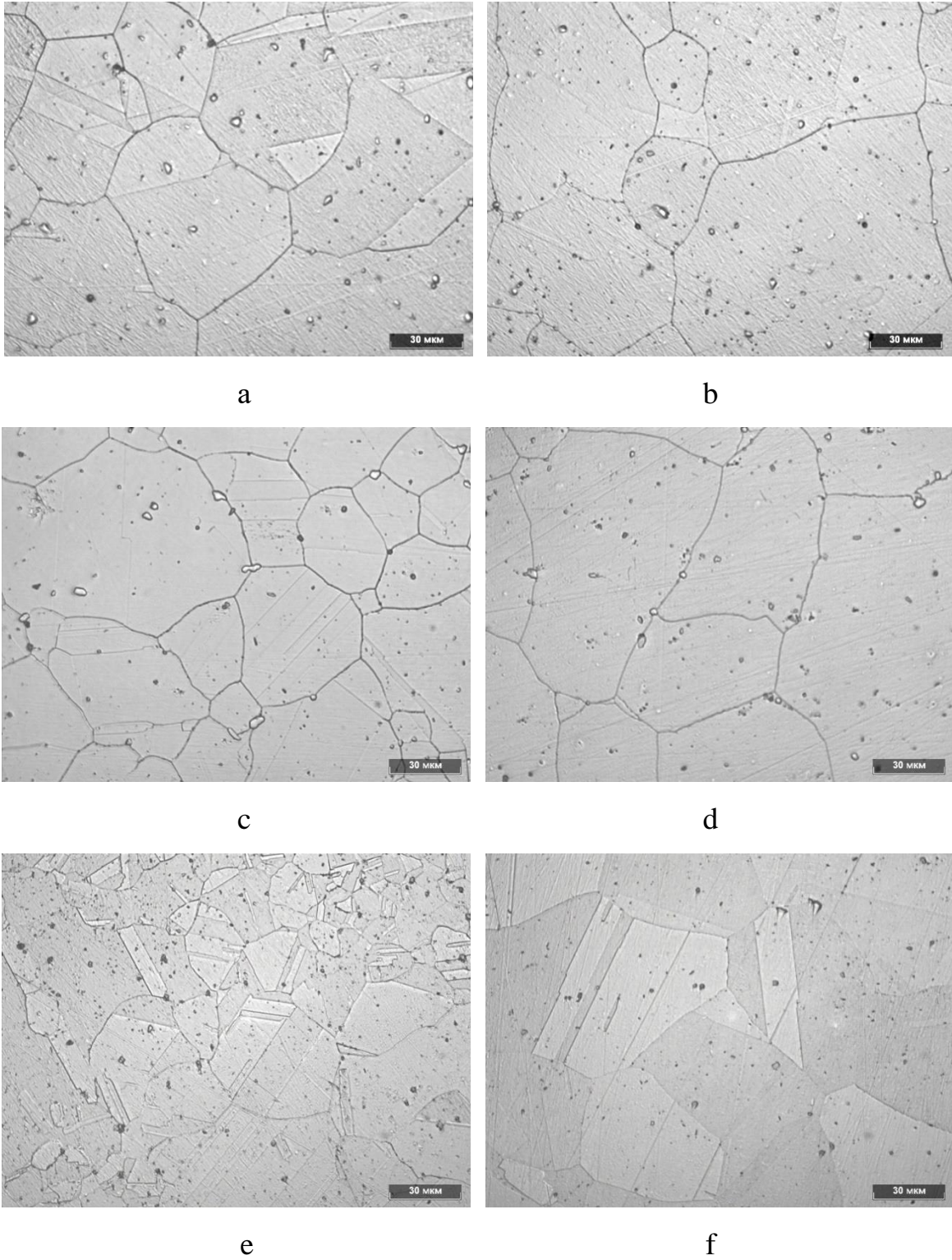
To determine the chemical composition of the structural components of the alloy electron microprobe was carried out. Analysis of the results showed that in the spectra obtained from the matrix of the alloys, in addition to the peaks of iron, nickel and carbon the peaks alloying elements: vanadium (in the alloy

32NF), vanadium, and molybdenum (in the alloy 34NFM) and vanadium and cobalt (in the alloy 32NFK ) are detected (Figure 3.17). Distribution map of chemical elements and micro roentgen spectra recorded from individual inclusions have demonstrated that carbon, vanadium, molybdenum, titanium are concentrated in them, but iron, nickel and cobalt are not almost detectable, which allowed the identification of such particles as carbides of the alloying elements.

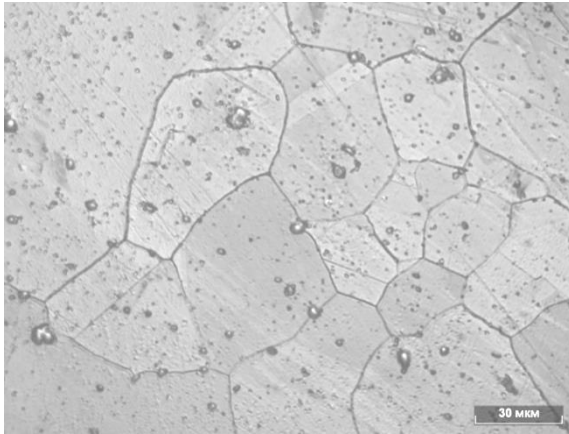


**Fig. 3.14** Electronic image of the investigated areas of the alloys microstructures 32NFK (a), and 34NFM (c), deoxidized according to the variant 5, and characteristic spectra (b, d), taken from the particles

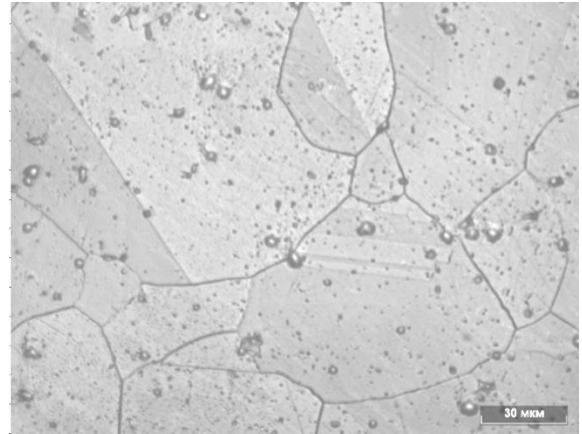




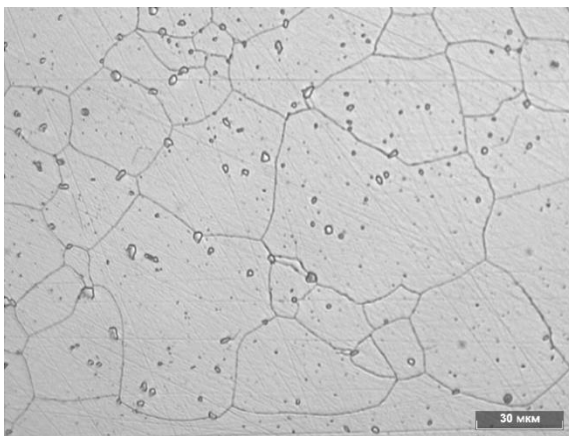
**Fig. 3.15** Microstructure 32NF alloys (a, b), 34NFM (c, d) and 32NFK (e, f) after quenching in water from 1200 ° C (a, c, e) and 1250 ° C (b, d, f) x 500



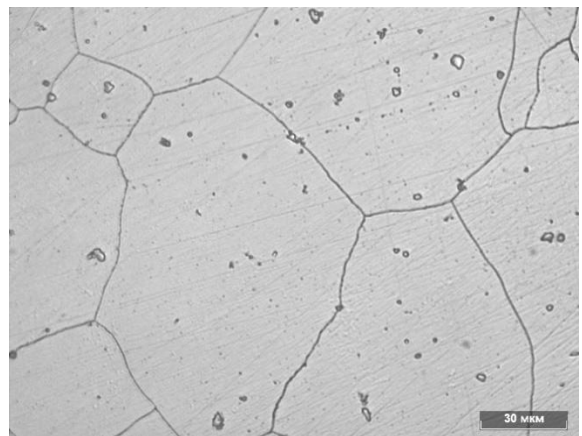
a



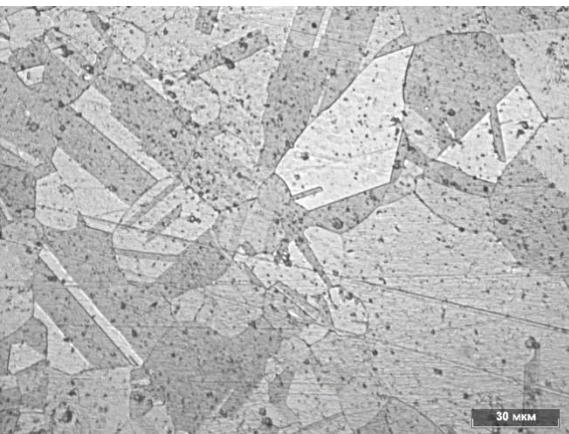
b



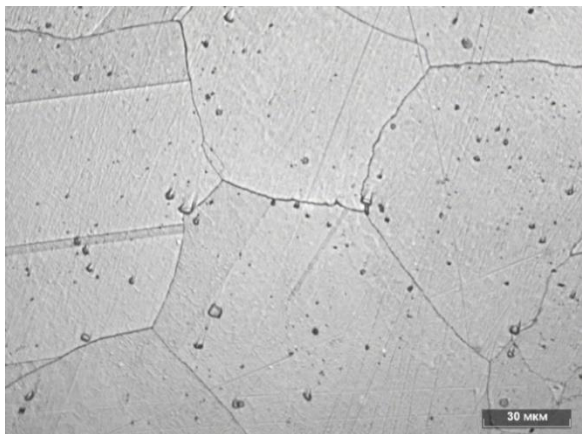
c



d

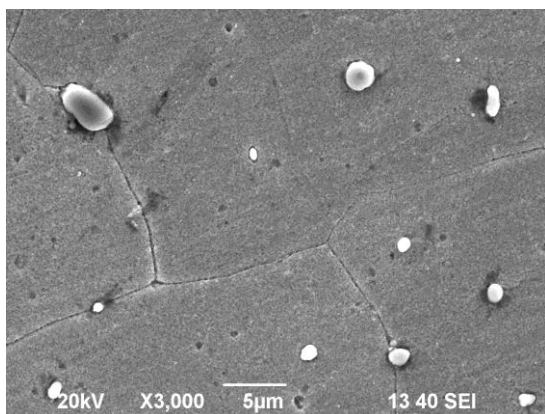


e

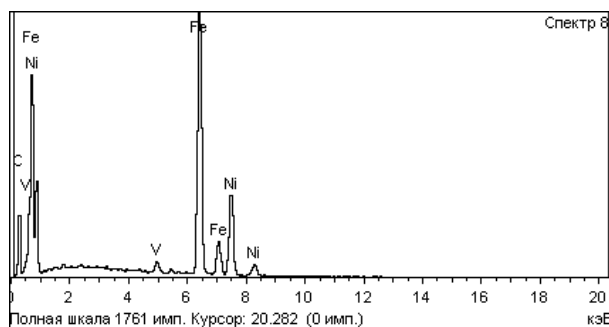


f

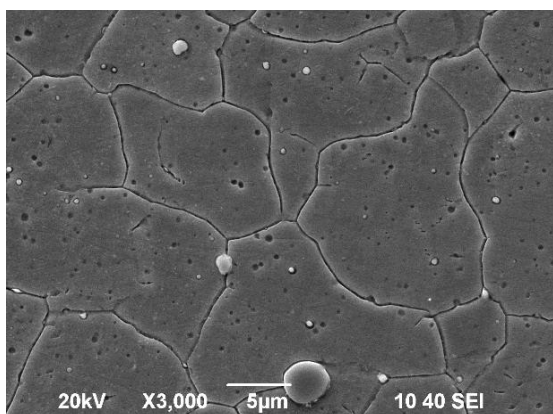
**Fig. 3.16** Microstructure of alloys 32NF (a, b), 34NFM (c, d) and 32NFK (e, f) after hardening in oil from 1200 ° C (a, c, e) and 1250 ° (b, d, f) x 500



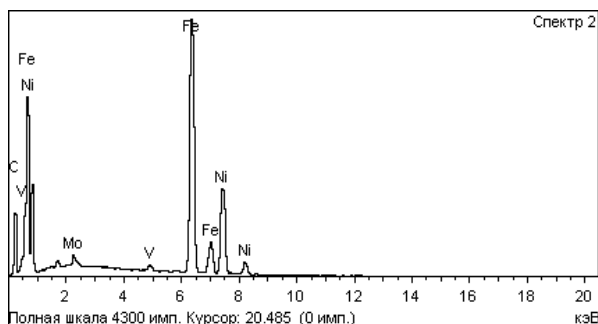
a



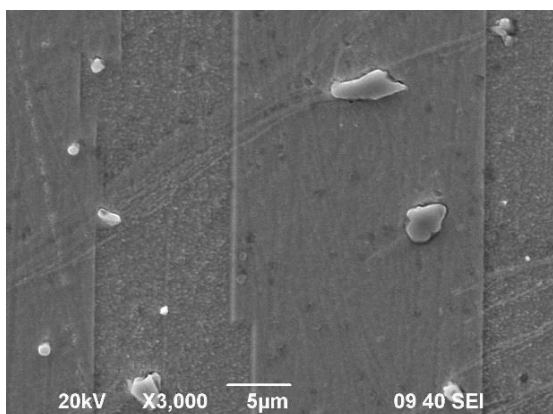
b



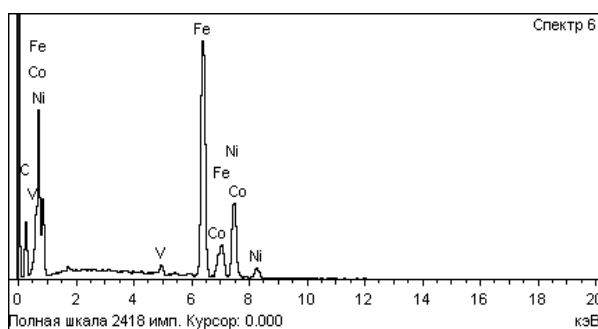
c



d



e



f

**Fig. 3.17** Alloy structure 32NF (a), 34NFM (c), 32NFK (e), quenched in water from 1200 ° C, and micro-roentgen spectra of the matrix (b, d, f)

Explanation of diffraction patterns obtained by the X-ray diffraction (XRD), showed that all the metal base of the alloys, as well as in the initial hot rolled state has the FCC lattice, i.e. polymorphic  $\gamma \rightarrow \alpha$  transformation during quenching is absent (appendixes 5-7). The diffraction patterns are recorded as peaks from crystallographic planes characteristic of carbides, which presumably can be identified as VC ( $V_4C_3$ ) (see appendixes 5-7).

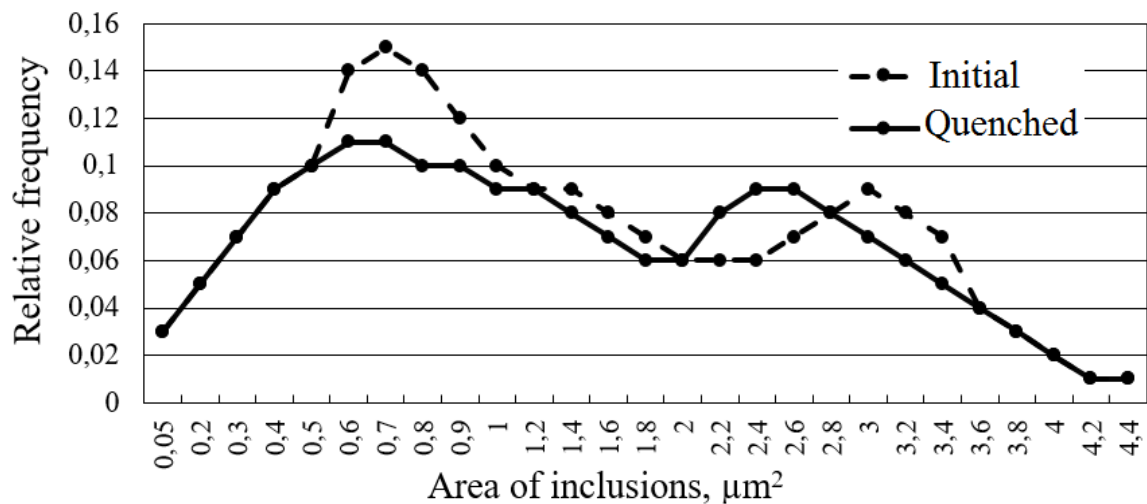
Quantitative analysis showed that by increasing the heating temperature for quenching the grain size of  $\gamma$ -solid solution increases. The average grain area of the alloys after quenching in various modes defined by the procedure described in section 2.6 is shown in Table 3.1.

**Table 3.1** Grain size of the alloys after quenching by different modes

Hardening mode	Average grain area, $\mu\text{m}^2$		
	32NF	34NFM	32NFK
1200 °C in oil	720	690	700
1200 °C in water	630	610	650
1250 °C in oil	1100	1050	2050
1250 °C in water	1000	970	1900

Determination of the particle size of the carbide phase was performed using the images obtained by the method SEM (see Section 2.6). According to the quantitative analysis of the frequency distribution curves of the inclusions sizes were built. Figure 3.18 shows the distribution area in the initial and quenched samples of the alloy 32NF.





**Fig. 3.18** Frequency curves of size distribution of nonmetallic inclusions of the initial and tempered alloy samples 32NF

According to the nature of the distribution it is possible to say that large carbides are partially dissolved, as evidenced by displacement of the characteristic maximum of average values of the area from the field of  $3 \mu\text{m}^2$  to around  $2.5 \mu\text{m}^2$ . The height of the peak which characterized the area of fine particles ( $0.7 \mu\text{m}^2$ ) became lower indicating a decrease in the number of dispersed carbide particles.

The distribution of particle sizes of the carbide phase for the rest of the investigated alloys is considered identical (square distribution graphs of inclusions of hardened samples are given further in Chapter 4).

According to the structure images obtained by SEM the quantitative analysis of the volume fraction of carbide inclusions in the microstructure of the quenched alloys was also carried out the results of which are presented in Table 3.2. On the basis on these data it is possible to make a conclusion that their amount decreases as compared with the initial state.

Thus, it can be concluded that by heating for hardening, the dissolution of the some part of carbide inclusions takes place. These inclusions were observed in

the original structure of the alloys. While quenching from a higher temperature of 1250 °C the greater number of inclusions were dissolved compared to quenching from 1200 °C.

**Table 3.2** Comparison of the number of particles of the carbide phase in the initial state and after hardening for various modes

Treatment	Quantity of carbide phase,%		
	32NF	34NFM	32NFK
The original hot-rolled condition	4.32	3.88	2.54
Hardening from 1200 °C in oil	3.4	3.12	2.11
Hardening from 1200 °C in water	3.12	2.92	1.85
Hardening from 1250 °C in oil	2.87	2.37	1.5
Hardening from 1250 °C in water	2.6	2.25	1.38

The method of the dilatometric analysis revealed that the dissolution of the carbide phase during heating for quenching begins at a temperature of 950-960 °C and continues during the isothermal holding, as evidenced by the characteristic inflections in the dilatometric curves of all the alloys.

The diffraction patterns of quenched samples shows a shift of characterized maximum from the crystallographic planes with the index (220) compared with the initial state (Figure 3.19). The changes in the crystal lattice parameters of the  $\gamma$ -solid solution, calculated on the basis of the X-ray diffraction results was also found, which indicates a change in alloying of the  $\gamma$ -solid solution by

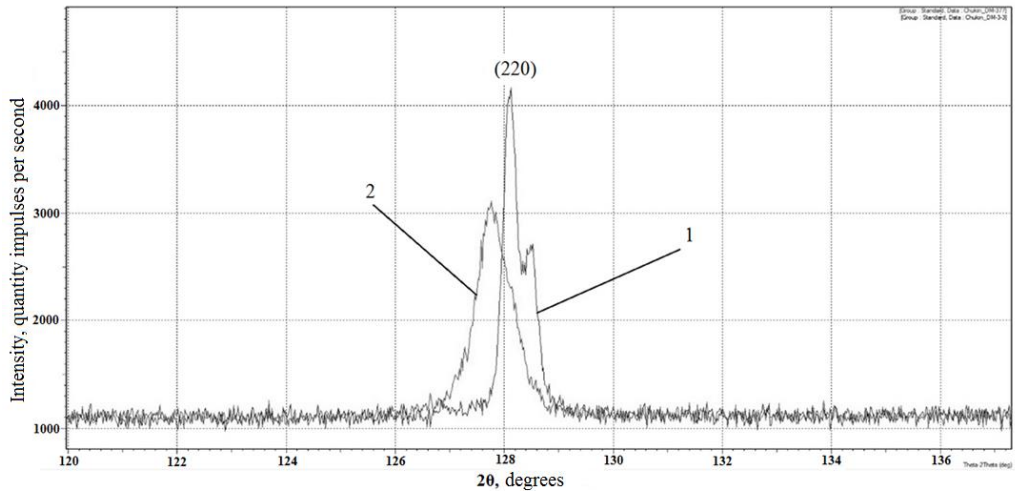
quenching (see. Appendix 4) as a result of the transition of carbon and alloying elements into it from the carbide phase, dissolved at heating.

It should be noted that complete dissolution of the carbide particles does not occur even when heated to 1250 °C. The authors of [57, 68, 69] by heating the Invar alloy Fe – 38% Ni – 1.0% Mo – 0.12% C – 0.27% Mn – 0.012% Si to temperatures of 1050-1200 °C also did not observe complete dissolution of carbides Mo<sub>2</sub>C, less resistant than vanadium carbides, which are mainly observed in the microstructure of the alloys.

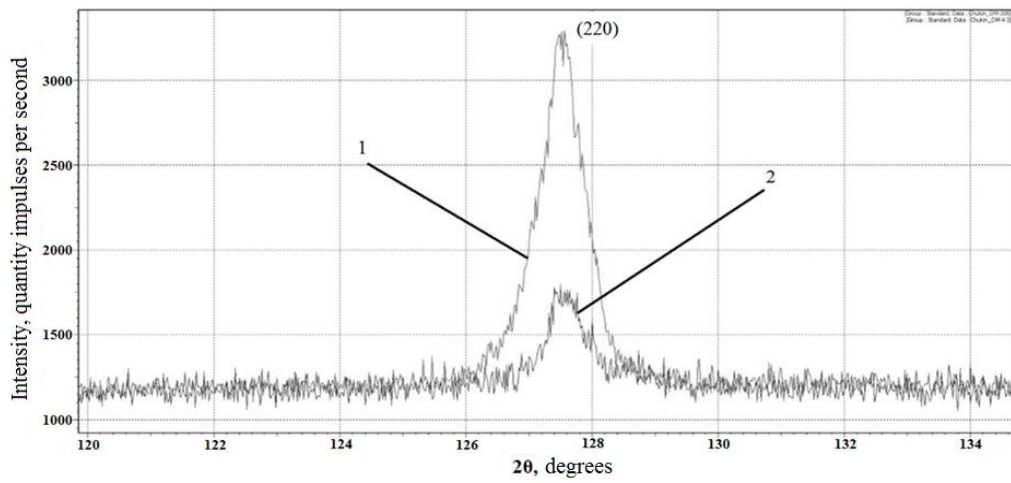
Results of hardness measurements, as illustrated in figure 3.20 show that, despite an appreciable grain growth with increasing heating temperature for quenching (see. Figures 3.15, 3.16), the hardness is not reduced in contrast to the data of the authors [68, 69], who observed a significant reduction in hardness with an increase in the grain growth. This is obviously due to a significant solid-solution strengthening by dissolving the carbides in the alloys which are under research in this work, with a high content of carbon and alloying elements - vanadium and molybdenum in them.

The highest hardness is obtained by quenching the alloy 32NF. It was by 30-40 HV higher than in the alloy 32NFK and 34NFM. This is because the alloy 32NF contains more carbon (0.76% - in the alloy 32NF and 0.4% - in the alloys 34NFM and 32NFK) and a greater amount of carbide phase (4.32% - in alloy 32NF, 3.88 % - in the alloy 34NFM and 2.54% - in the alloy 32NFK). Therefore, when heated for quenching of the alloy 32NF dissolution of the carbide phase takes place and carbon is transferred into a solid solution, it increasingly hardens it.

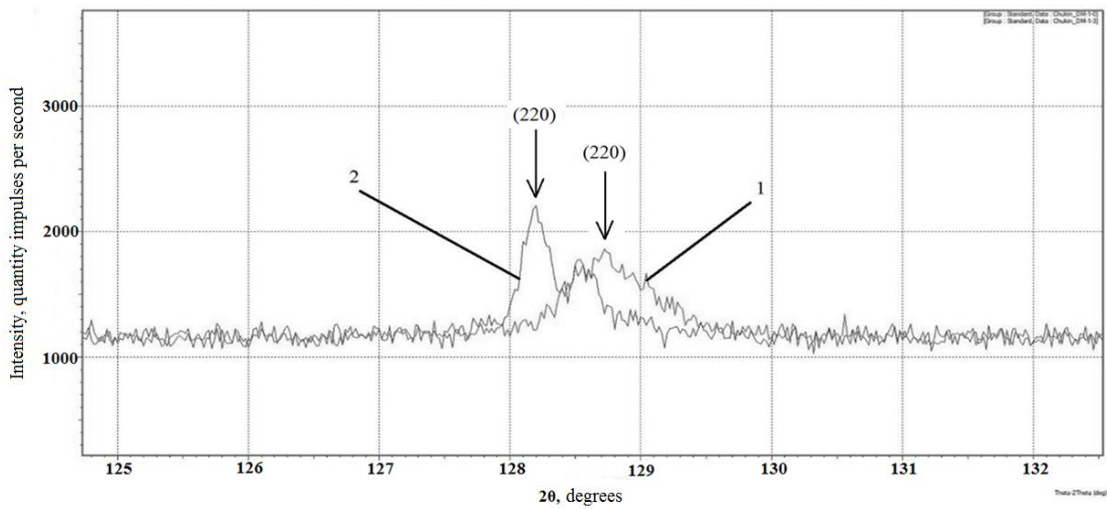
Hardness of the quenched alloy 34NFM, in its turn, appeared to be higher than the hardness of the alloy 32NFK. With the same carbon content (0.40%) and about the same content of vanadium (1.4 and 1.46%) the amount of the carbide phase in the alloy 34NFM is greater than in the alloy 32NFK. In this regard,



a



b

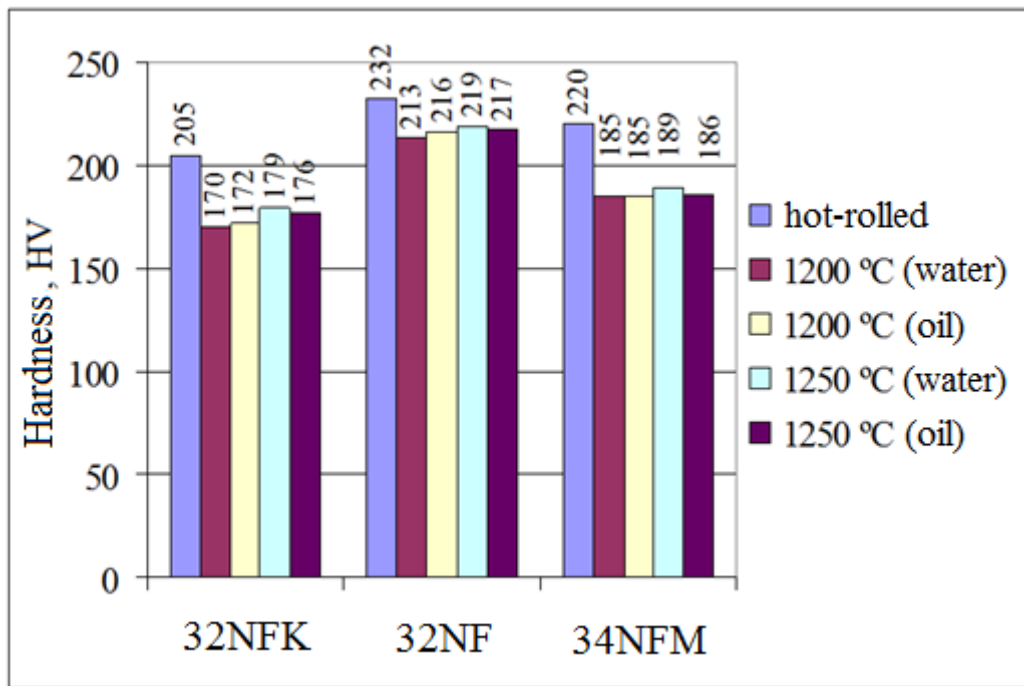


c

**Fig. 3.19** Characteristic maxima (220) for the alloy 32NF (a), 34NFM (b), 32NFK (c) in hot-rolled (1) and quenched states (2)



during heating for quenching upon dissolution of the carbide phase solid solution is further saturated by carbon and molybdenum, thereby providing a more solid-solution strengthening. Thus, molybdenum is more effective for increasing the hardness by quenching as compared with cobalt additions in the alloys Fe-Ni-C.



**Fig. 3.20** The hardness of Invar alloys in the initial hot rolled condition and after quenching in various modes

### Conclusions on Chapter 3

1. New scientific data on the effect of the chemical composition of deoxidizers on the structure of high-strength Invar alloys have been obtained. Based on the results of microscopic, electron microscopy and electron microprobe, it was found that the most suitable deoxidizer composition is: 0.15% Mn<sub>ref</sub>, 0.35% NiMg (0.15% Mg), 0.1% Si<sub>cr</sub>, 0.1 % SiCa, 0.06% Al and 0.07-0.1% Ti<sub>sponge</sub> that

provides fewer, smaller, and the most favorable form of non-metallic inclusions of metallurgical origin.

2. The features of the structure of hot-rolled Invar alloys of the Fe-Ni-C-V, Fe-Ni-C-Co-V, Fe-Ni-C-V-Mo systems, showing that the major structural elements in them are gamma-solid solution with FCC lattice doped with cobalt, vanadium and molybdenum and carbides containing vanadium and / or molybdenum.

3. It was established that during heating for quenching, the dissolution of the part of the carbide phase and the saturation of the solid solution with carbon and carbide-forming elements: vanadium and molybdenum takes place. However, to receive the full state of a single-phase alloy ( $\gamma$ -solid solution) even when heated to 1250 °C is not possible, and some part of carbides remains undissolved. It is shown that when quenching from a higher temperature of 1250 °C a greater number of inclusions are dissolved compared to quenching from 1200 °C and there is a marked grain growth, thus increasing the quenching temperature to 1250 °C is not accompanied by a decrease in hardness.

4. The highest hardness obtained by quenching of the alloy 32NF has been obtained. It appears to be 30-40 HV higher than the alloys 32NFK and 34NFM, due to the higher carbon content in the alloy 32NF and its determining role in strengthening.

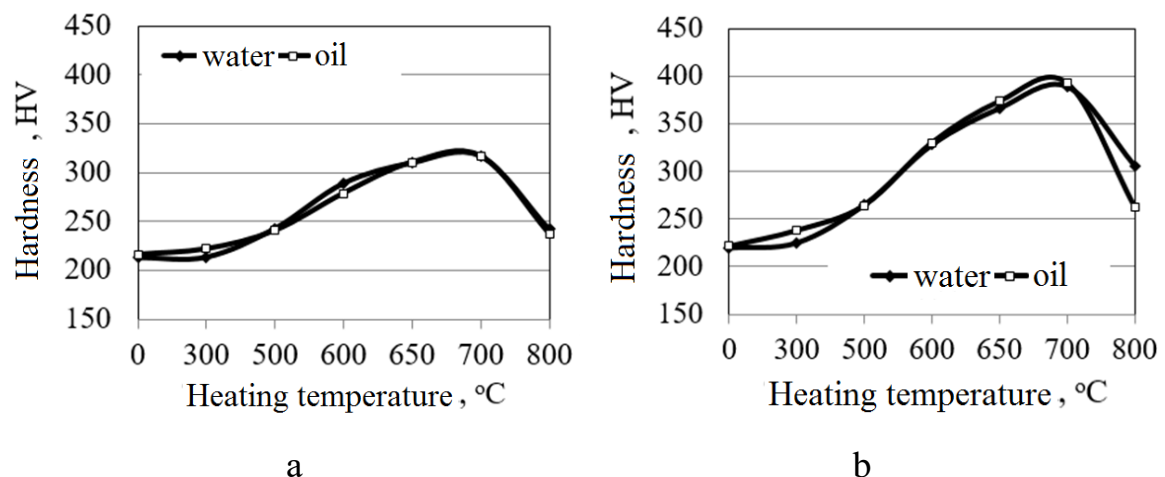
5. Molybdenum is more effective for increasing the hardness by quenching in comparison with the additives cobalt of due to the formation of the added amount of the carbide phase, the dissolution of which upon heating for quenching enriches the solid solution with carbon and molybdenum, promoting solid-solution strengthening.

# CHAPTER 4

## STRUCTURAL CHANGES AND MECHANICAL PROPERTIES AT AGING THE QUENCHED INVAR ALLOYS

### 4.1 The researches of microstructure and mechanical properties after aging the alloy 32NF and discussion

Hardness test results after heating 32NF alloy samples previously quenched from 1200 to 1250 °C in water and oil, are shown in Figure 4.1. It indicates that the increase in temperature of heating the quenched alloys from 300 to 700 °C is accompanied by increased hardness. The largest hardness of the alloy 32NF is achieved by heating to 700 °C (400 HV), at the same time ultimate strength was 1150 N/mm<sup>2</sup> and yield strength - 1020 N/mm<sup>2</sup>. By further heating temperature increasing to 800 °C the hardness decreases on 90-110 HV and strength on 300-400 N/mm<sup>2</sup>.



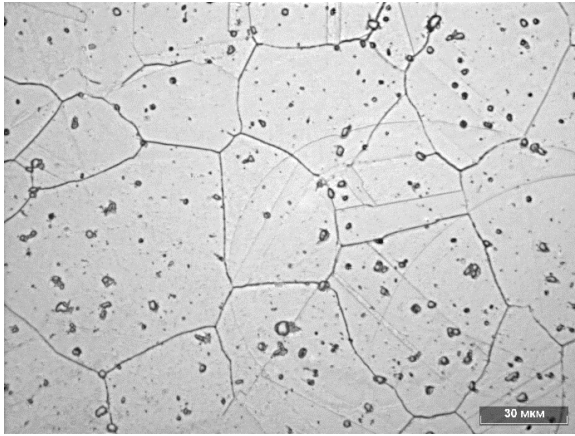
**Fig. 4.1** Change of hardness on heating 32NF alloy pre-quenched from 1200 °C (a) and 1250°C (b)

The hardness after samples heating quenched with more high temperature was about on 80 HV and ultimate strength - 300-400 N/mm<sup>2</sup> more than properties of samples quenched with more low temperature 1200 °C. At the same time the strength of the samples quenched in water and in oil differed insignificantly.

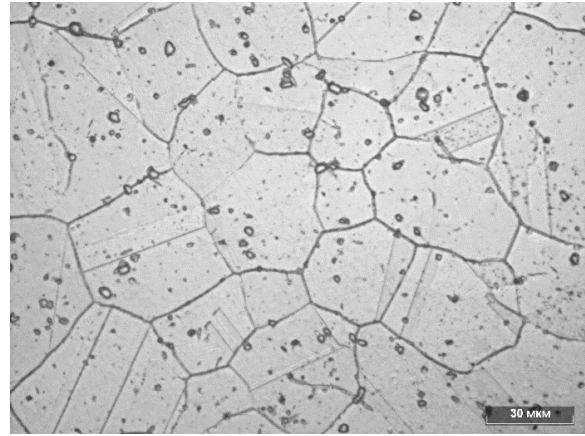
The alloy 32FN microstructure after heating of samples quenched from 1200 to 1250 °C in water and in oil is shown on Figures 4.2 and 4.3. The results of light microscopic analysis showed that in all the cases after quenched samples heating the microstructure consists of different size grains of metal base and disperse or more large particles. A cooling medium used during the quenching doesn't significantly influence on structure after heating. At the same time the heating of samples, previously quenched with 1250 °C, lesser quantity of large particles and more large grain of metal base is observed as opposed to samples, previously quenched with 1200 °C.

The large particles as shown earlier are vanadium carbides, which didn't completely dissolve during heating for hardening. Besides it disperse particles are observed, which quantity raises by temperature increasing from 300 to 700 °C (Figure 4.4). The analysis of images performed by the SEM method showed that during heating of the samples quenched from 1250 °C, the number of dispersed particles more than in the structure of samples quenched from 1200 °C (see Figure 4.4).

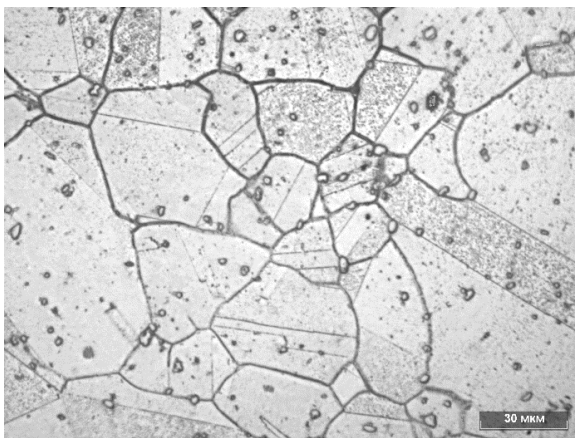
To identify the chemical elements enter into the composition of structural components of the alloy, electron microprobe analysis was conducted, the results of which is illustrated in Figure 4.5. In the spectra obtained from the metal base (Figure 4.5, a, b), as expected, were detected peaks of iron, nickel, carbon and vanadium. In the spectra from large particles, which were observed in the alloy after quenching, were detected peaks of carbon, vanadium and titanium (Figure 4.5, c, d). The presence of titanium in the composition of large carbides is due to the fact that titanium is used in the composition of the



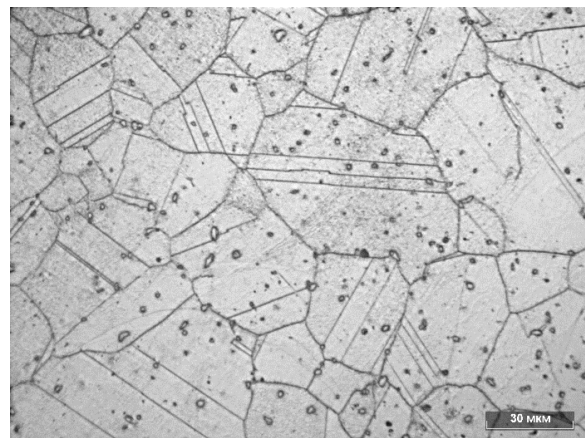
a



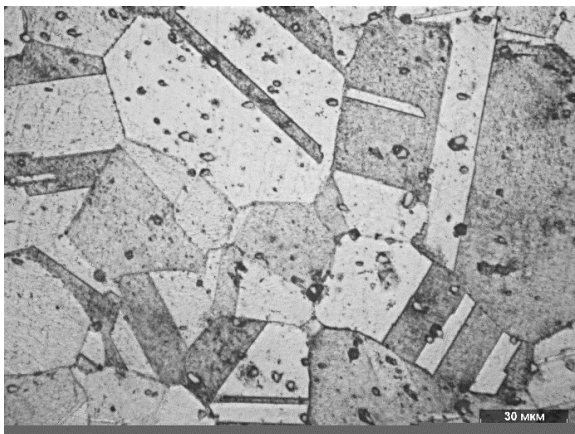
b



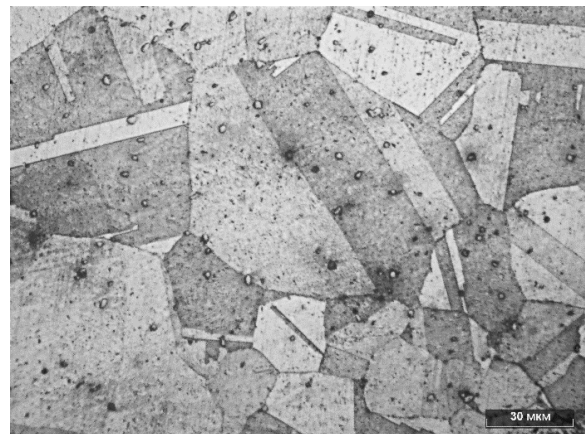
c



d



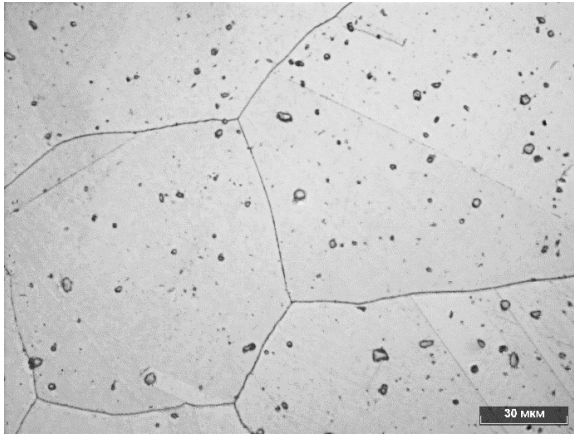
e



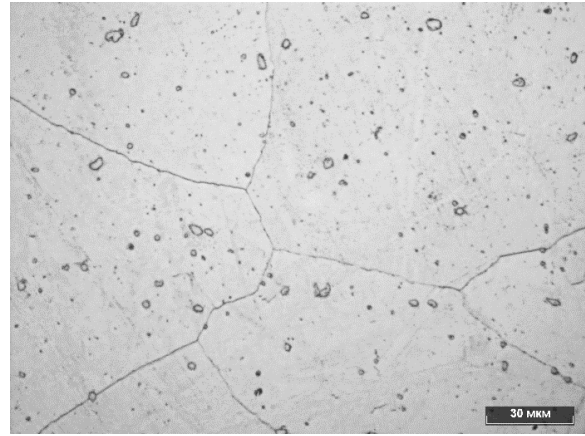
f

**Fig. 4.2** Microstructure of the alloy 32NF after heating to 300 °C (a, b), 650 °C (c, d) and 800 °C (e, f) samples pre-quenched from 1200°C in water (a, c, e) and in oil (b, d, f), x 500

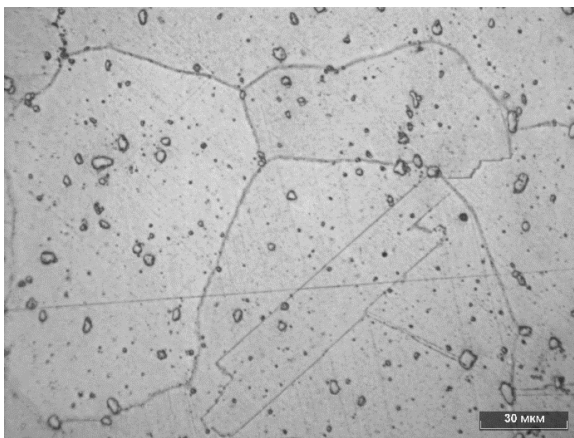




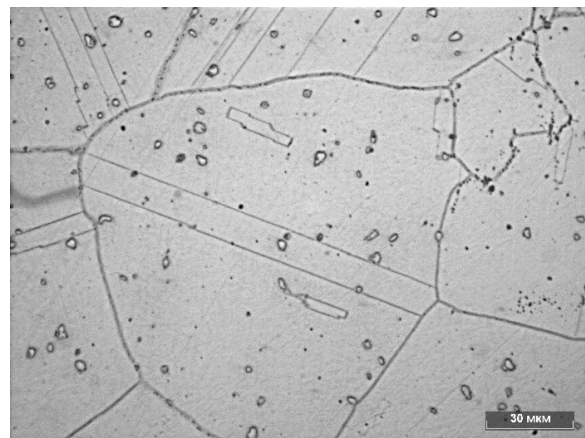
a



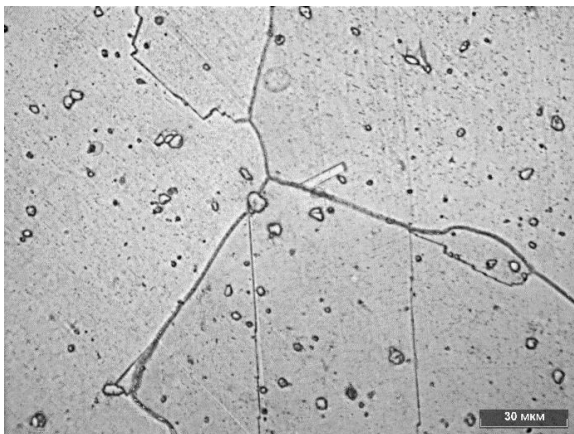
b



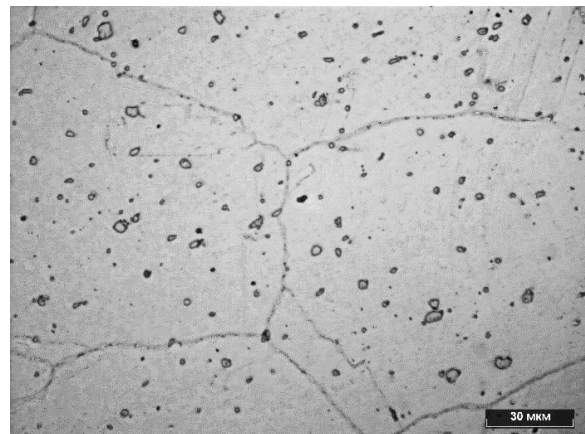
c



d



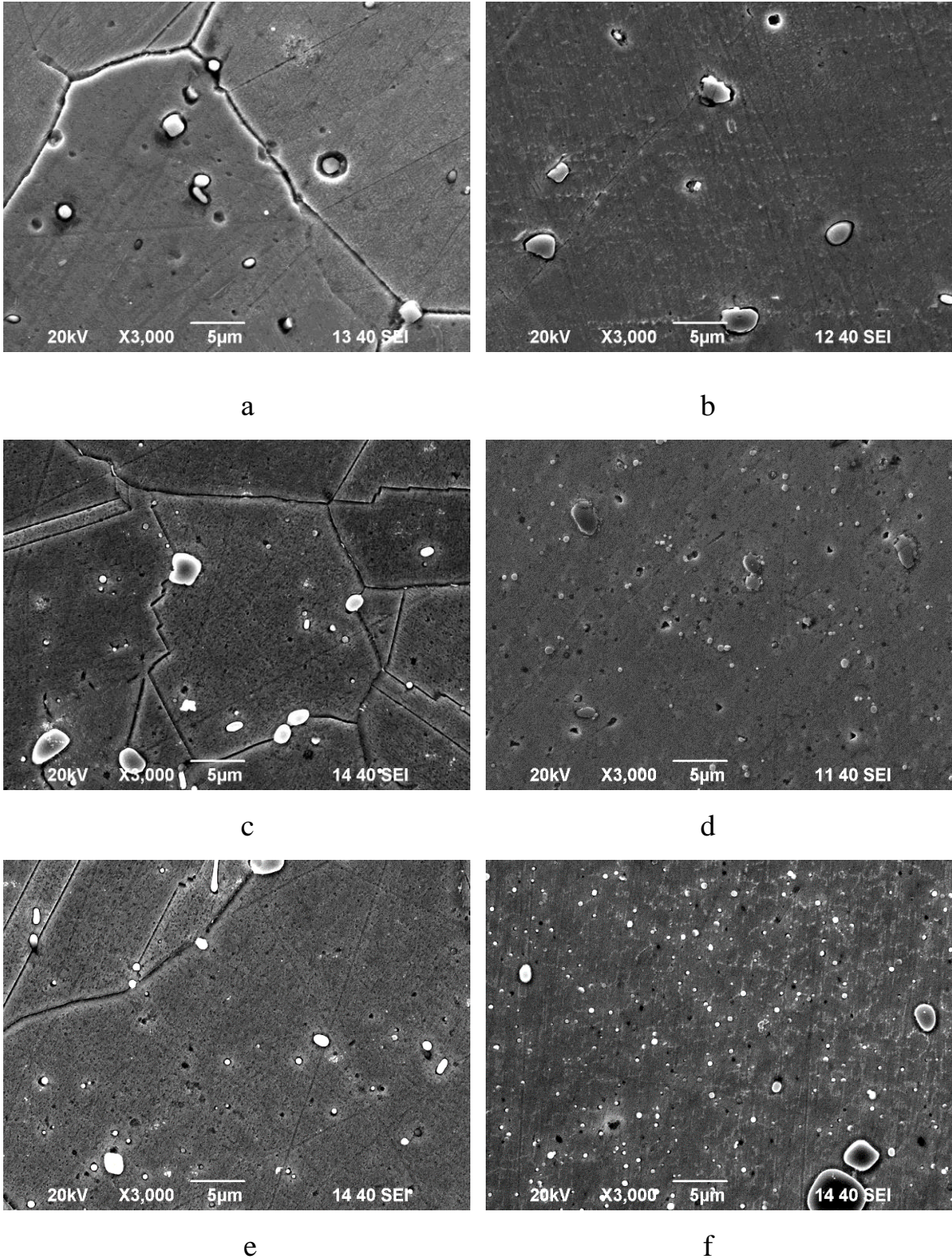
e



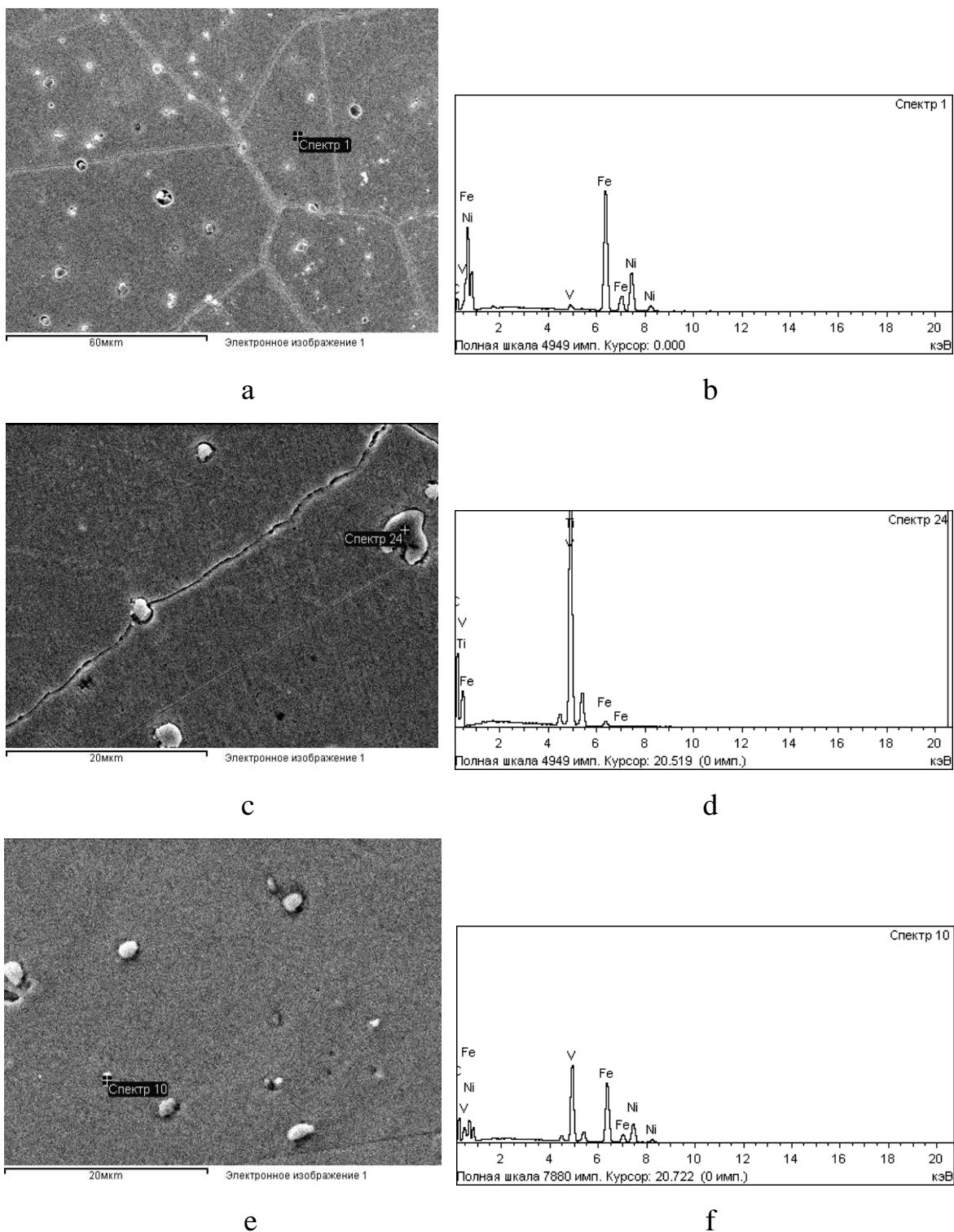
f

**Fig. 4.3** Microstructure of alloy 32NF after heating to 300 °C (a, b), 650 °C (c, d) and 800 °C (e, f) samples, quenched from 1250 °C in water (a, c, e) and in oil (b, d, f), x 500





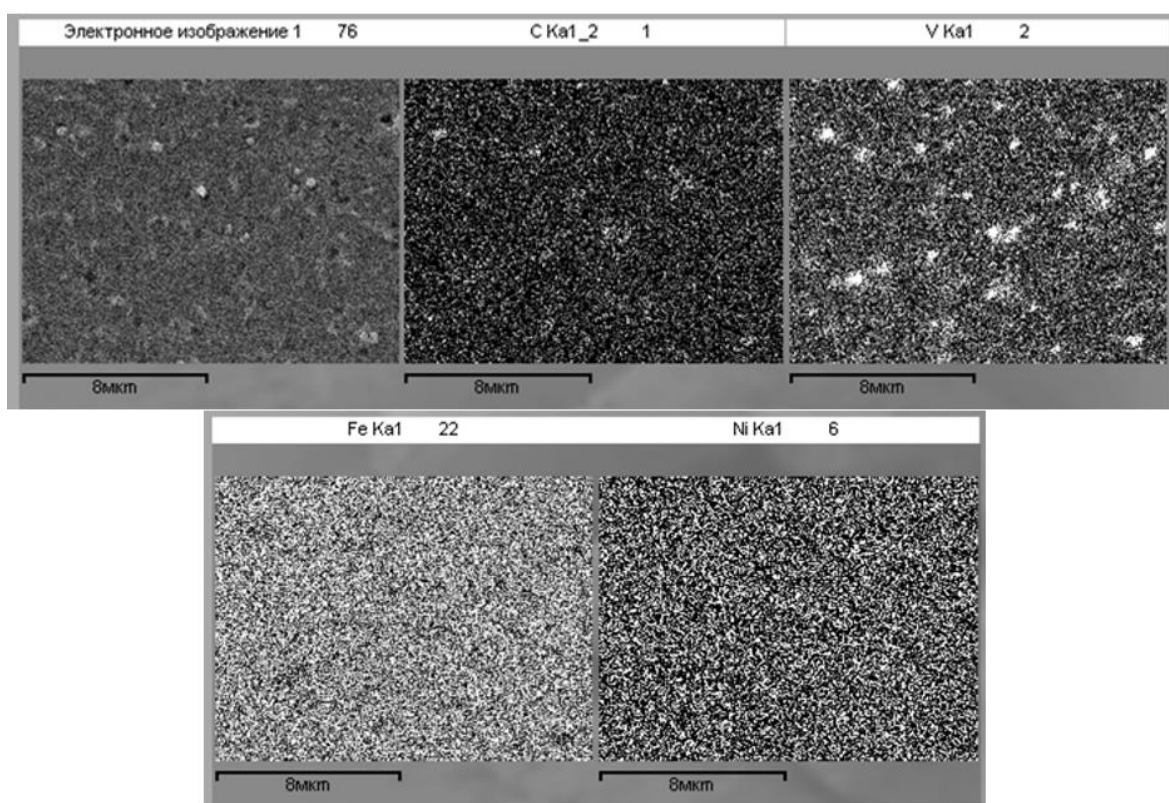
**Fig. 4.4** Electronic microscopic image of the microstructure of the alloy 32NF after quenching from 1200 °C (a, c, e) and 1250 °C (b, d, f) in water and heating at 300 °C (a, b), 500 °C (c, d) and 700 °C (d, e)



**Fig. 4.5** Electronic image of the microstructure of the alloy 32NF after heating at 700 °C(a, b, d) and the characteristic spectra from these areas of the matrix (b) large particles (d) dispersed particles (e)



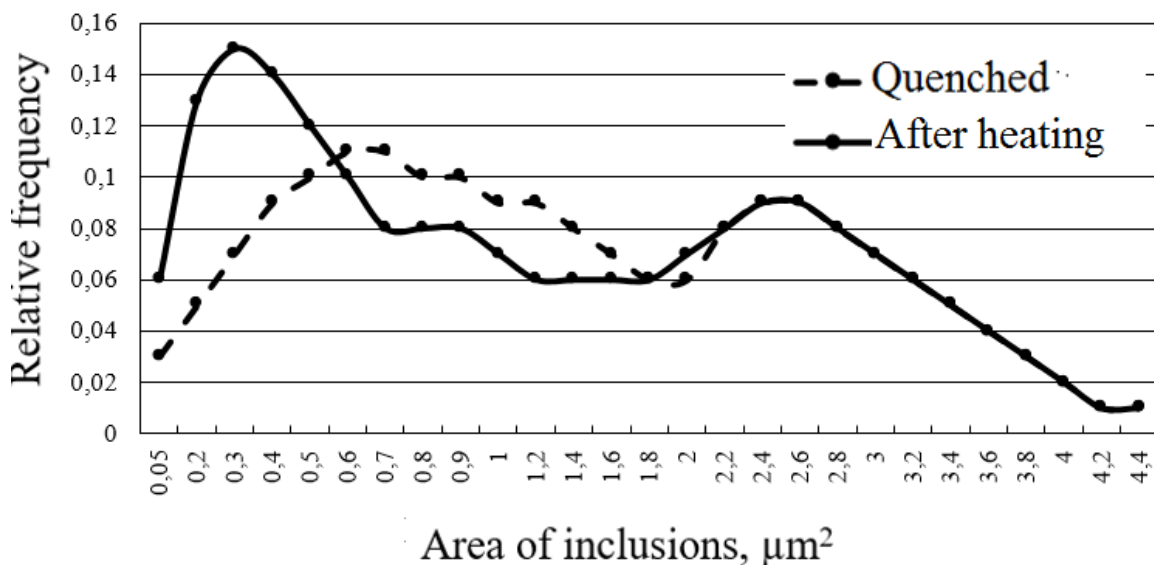
deoxidizer, and being the strongest carbide-stabilizing element that fixes the carbon in the resistant carbides, which isolated by crystallization and not completely dissolve during heating for hardening. In the spectra taken with dispersed inclusions, there are peaks of carbon and vanadium (Figure 4.5, e, f). Distribution maps of the elements confirmed that there are concentrations of vanadium and carbon in the separated dispersed particles (Figure 4.6). Thus it can be concluded that the observed particles are the carbides of vanadium. It should be noted that the regions enriched with vanadium are observed in the areas in which in the electronic image of the structure of particles is not detected. This can be explained by the fact that in the process of making micro sections of dispersed carbide particles fall out of the matrix.



**Fig 4.6** Electronic image of the microstructure of the alloy 32NF after heating at 700 °C and the distribution pattern of carbon, vanadium, iron and nickel

By decoding the diffraction patterns obtained with XRD of the samples of alloy 32NF after heating, the peaks are recorded from crystallographic planes, which are characterized for carbides, which supposedly can be identified as VC ( $V_4C_3$ ) (Appendix 8), which confirms the conclusion above. The obtained results are consistent with the existing literature data on the dispersion hardening during the decomposition of solid solution in Fe-Ni invar alloys [39, 63, 65, 69, 85].

According to a quantitative analysis using images obtained by SEM (see section 2.6), curve of the frequency density distribution of the sizes of the carbides after heat-treatment was built, which ensured the highest hardness of the alloy 32NF - after heating to 700 °C samples, previously quenched with 1250 °C in water (Figure 4.7, solid line). The frequency of occurrence of an event is observed on the ordinate, expressed in arbitrary units, the abscissa shows the square of the particles of the carbide phase. For comparison curve of density distribution of the particle sizes of sample of the same alloy hardened from 1250 °C in water built on the same graph.



**Fig. 4.7** Distribution of particle sizes of carbides in the microstructure of alloy 32NF after quenching and heating to 700 °C

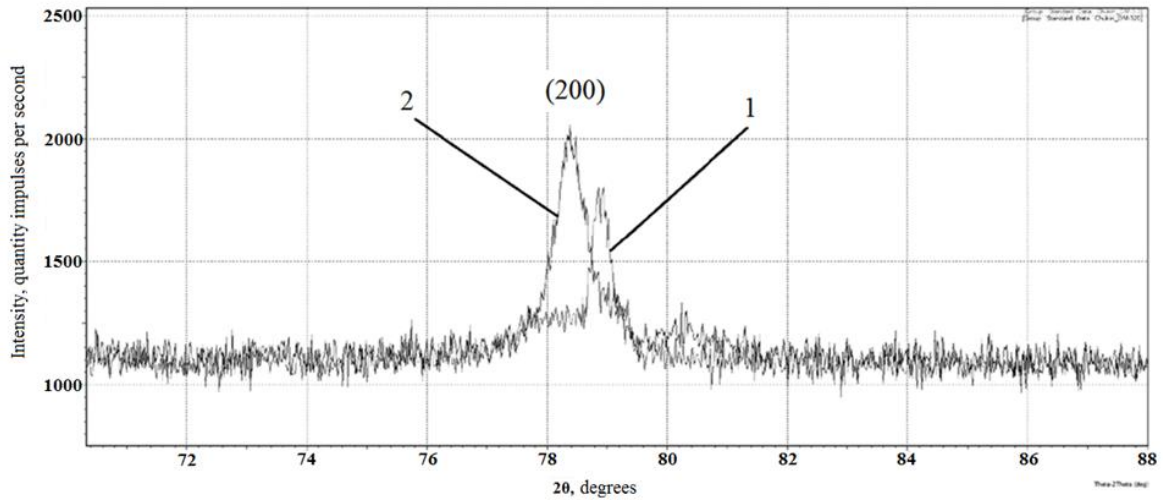
Analysis of the obtained curves, both in the tempered condition and after aging, shows two peaks that characterize the large and dispersed particles of carbides. The height and position of peak indicates the relative number of large particles has not changed, that means the relative proportion of large particles size from 2.4 to 2.6  $\mu\text{m}^2$  stayed the same. The peak characterizing the relative quantity of disperse particles in the hardened condition (0.7  $\mu\text{m}^2$ ) after heating increased height and displaced to the left in the region an average area of 0.3  $\mu\text{m}^2$ . This indicates that the increasing in the number of disperse carbide inclusions is observed with heating, which occurs as a result of their isolation from saturated with carbon and vanadium solid solution obtained by quenching.

Thus, we can conclude that the processes of aging are observed by heating the pre-quenched alloy 32NF and the temperature range from 300 to 700 °C, accompanied by increasing the hardness in the result of the dispersion hardening with the carbides of vanadium isolation.

Decryption of diffraction patterns obtained XRD confirmed, that the metal base is a  $\gamma$ -solid solution with the FCC lattice (Appendix 8). It was found that after aging the pre-quenched alloy samples 32NF a shifting of the characteristic maximum of the reflection that is shown in the overlay of diffraction patterns from quenched and aged samples (Figure 4.8).

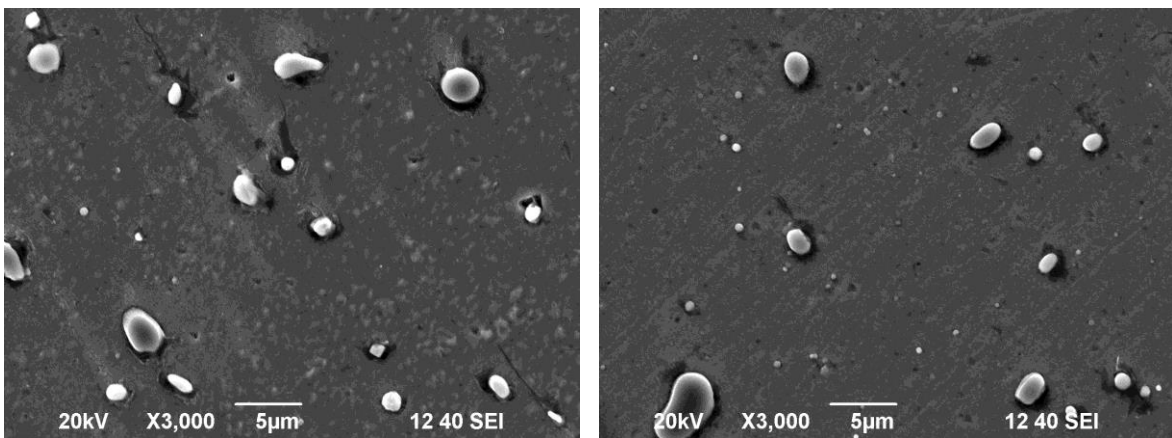
The calculated lattice parameter in comparison with quenched condition has changed, that indicates a change in alloyed  $\gamma$ -solid solution during aging as a result of transition atoms and vanadium carbon in the carbide phase. The characteristic changes of the dilatometric curves slope angle was documented by the method of dilatometric analysis (see Chapter 5), which also indicates the isolation of disperse carbide particles during aging. Higher temperature of heating for hardening provides a more complete dissolution of the initial carbide particle, greater saturation of the solid solution with carbon and

vanadium and, consequently, a greater effect of dispersion hardening by its disintegration, which explains the higher hardness of the alloy 32NF, pre-hardened from 1250 °C (see Figure 4.1).



**Fig. 4.8** Typical highs (200) for the quenched sample of the alloy 32NF (1) and sample after aging at 700 °C (2)

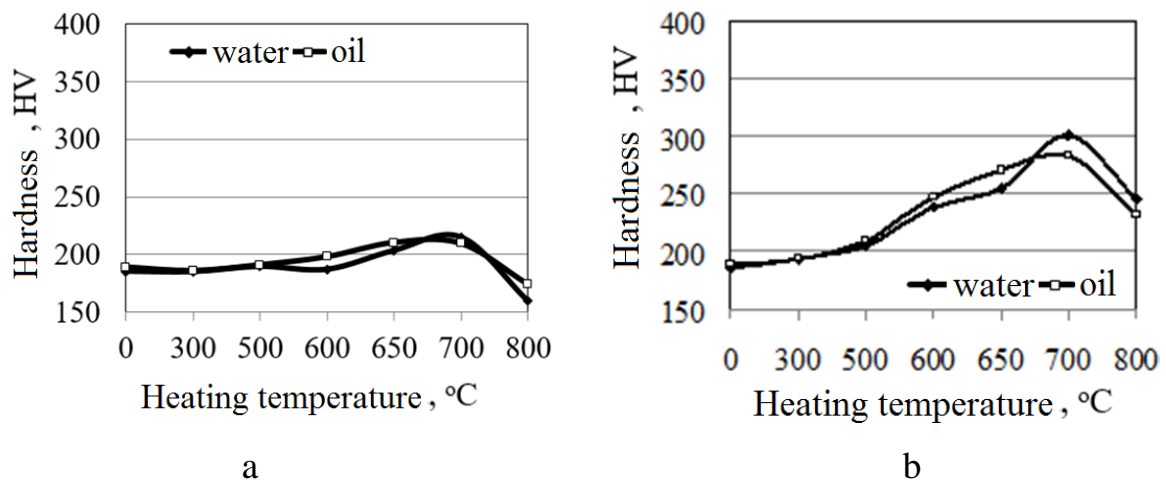
The decreasing in hardness with increasing the aging temperature to 800 °C is due to the coagulation of the carbide particles, as was demonstrated by the microstructural studies (Figure 4.9).



**Fig. 4.9** Structure of 32NF alloy after quenching from 1250 °C and heating at 800 °C for 1 h

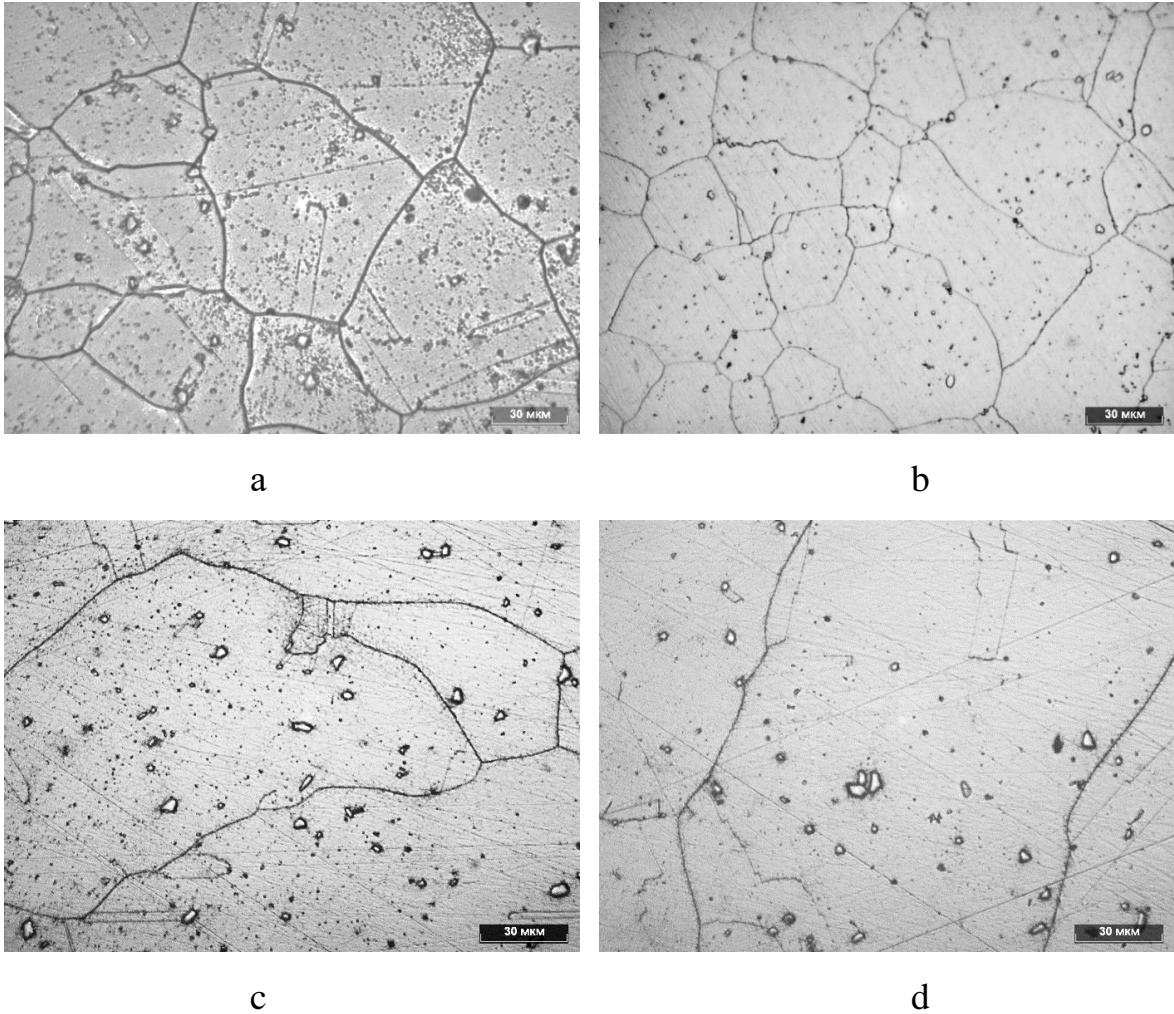
#### 4.4 The researches of the microstructure and mechanical properties after aging alloy 34 NFM and discussion

Hardness change during heating of samples of the alloy 34NFM, previously quenched from 1200 and 1250 °C in water and in oil, illustrated in Figure 4.10. The increasing temperature from 300 to 700 °C, as in the case of the alloy 32NF, accompanied by increasing in hardness. The highest hardness of 300 HV in the alloy 34NFM is achieved by heating and aging at 700 °C, while the tensile strength amounted to 870 N/mm<sup>2</sup> and a yield strength of 780 N/mm<sup>2</sup>. With further increasing of heating temperature to 800 °C decreases the hardness by about 70 HV and strength about 150-200 N/mm<sup>2</sup>.



**Fig. 4.10** Change of hardness on heating 34NFM alloy pre-quenched from 1200 °C (a) and 1250°C (b)

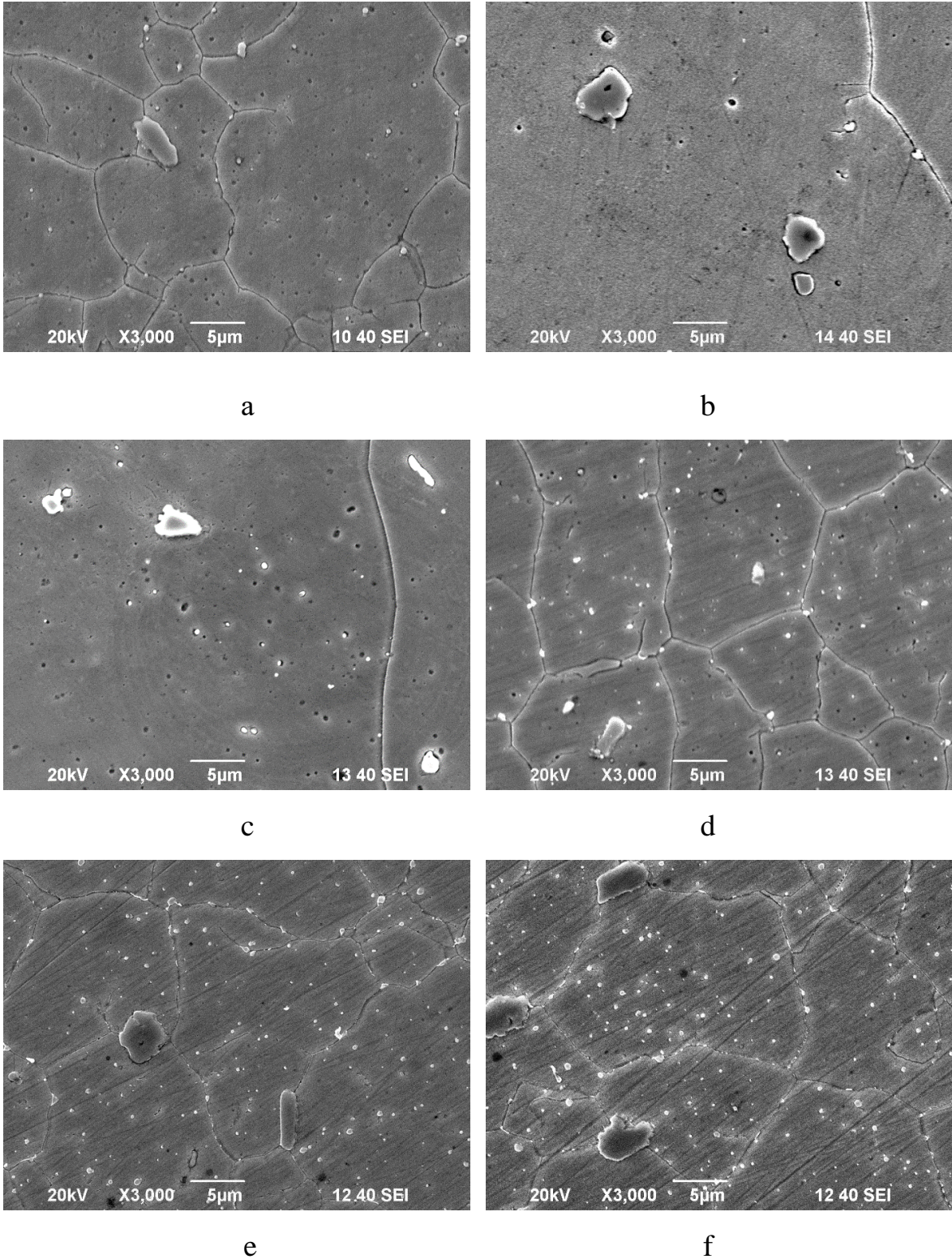
The microstructure of the alloy 34NFM after heat treatment for maximum hardness, as shown in Figure 4.11. It is a grain metallic substrates of different sizes with large and dispersed particles. Quenching from higher temperatures leads to grain growth and reduction in the number of particles, and the cooling medium has not a strong influence on the nature of the structure.



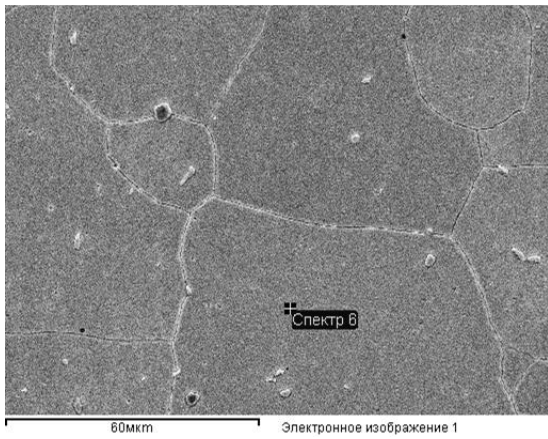
**Fig. 4.11** Microstructure of the alloy 34NFM after heating at 700 °C of samples quenched from 1200 °C (a, b) and 1250 °C (c, d) in water (a, c) and in oil (b, d), x 500

Results showed by SEM (Figure 4.12) that the number of dispersed particles of spherical shape increases with increasing temperature from 300 to 700 °C. Microprobe analysis of typical results which is illustrated the figures 4.13 and 4.14 showed that in the spectra obtained from the metal base (Figure 4.13 a, b) detected peaks of iron, nickel, carbon, vanadium and molybdenum. In the spectra from large particles, which were observed in the alloy after quenching, the detected peaks of carbon, titanium, vanadium and molybdenum (see figure 4.5, c, d). As noted above, the presence of titanium is due to the fact, that

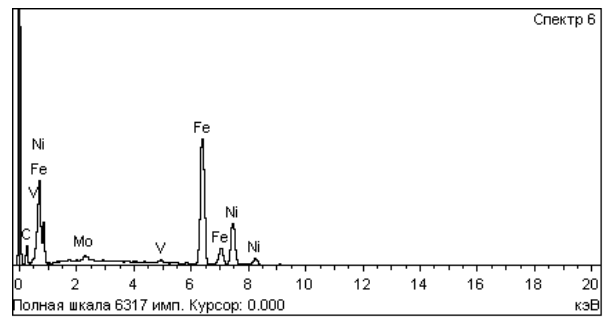




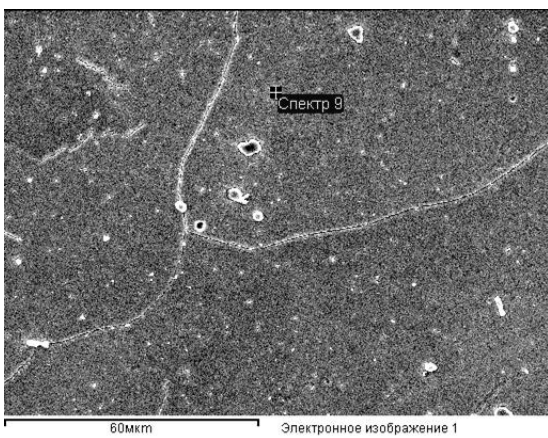
**Fig. 4.12** Electronic microscopic image of the microstructure of the alloy 34NFM after quenching from 1200 °C (a, c, e) and 1250 °C (b, d, f) in water and heating at 300 °C (a, b), 600 °C (c, d) and 700 °C (e, f)



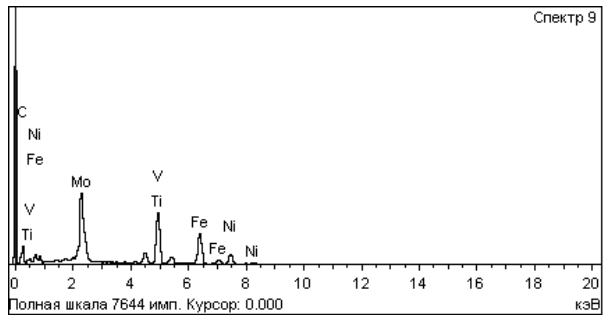
a



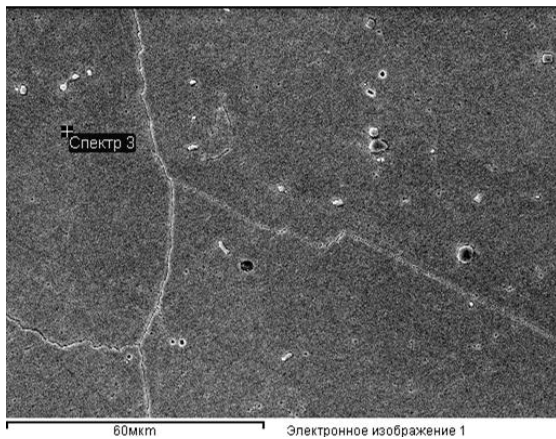
b



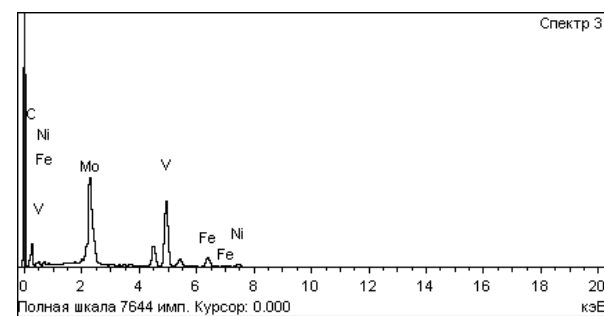
c



d



e

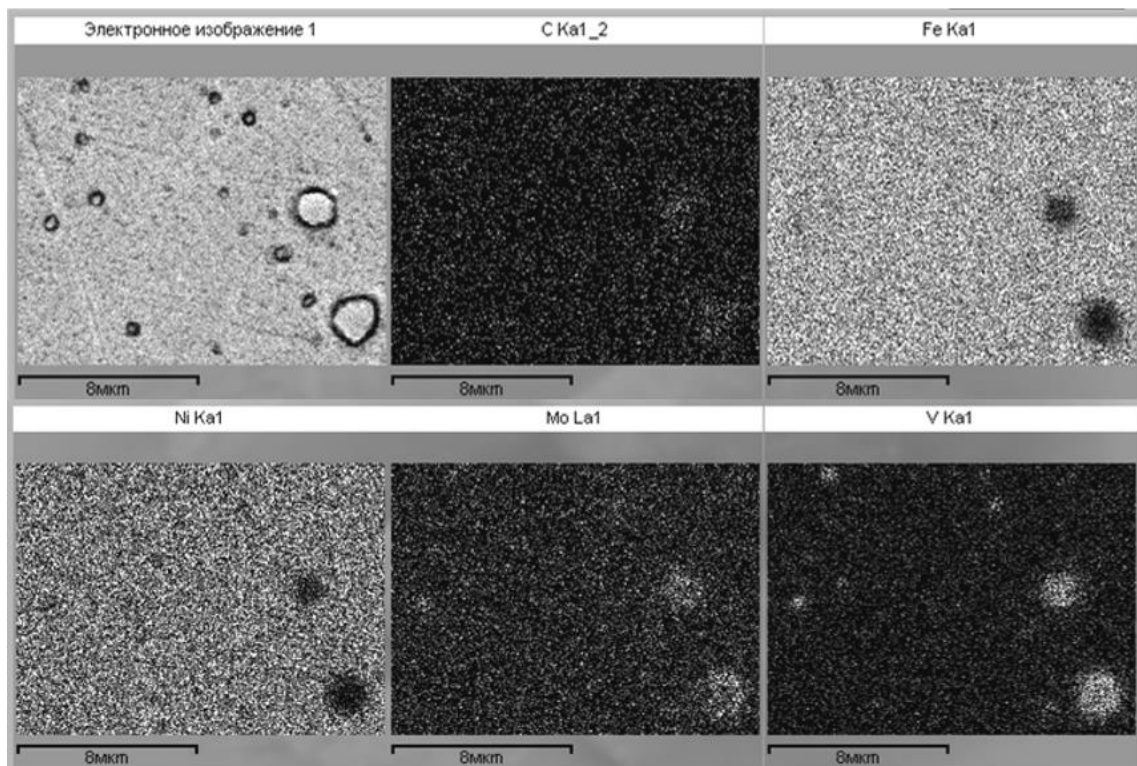


f

Figure 4.13 - Electronic image of the microstructure of the alloy 34NFM after heating at 700 °C (a, c, e) and the characteristic spectra from these areas of the matrix (b) large particles (d), the disperse particles (f)

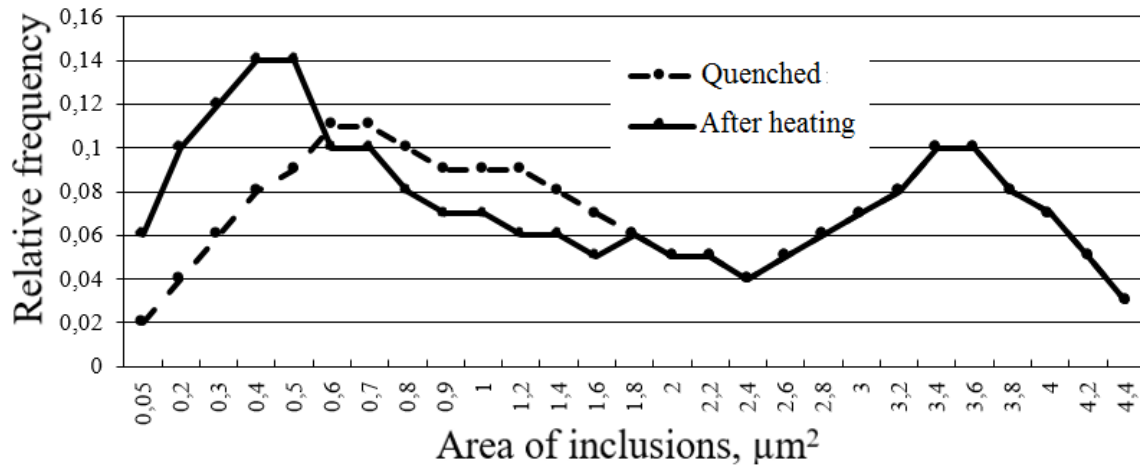


titanium is used in the composition of the deoxidizer, and being the strongest carbide-stabilizing element that binds the carbon in the resistant carbides, which are isolated during crystallization and don't not completely dissolve during heating for hardening. In the spectra taken with disperse inclusions, there are peaks of carbon, vanadium and molybdenum (Figure 4.13 e, f). On the basis of microprobe analysis can be argued that the second phase particles are carbides containing molybdenum and vanadium. The most small carbide particles don't contain titanium, which is an indirect proof of their isolation in the heating process. Maps of elements distribution(Figure 4.14) confirmed that after heating the vanadium is concentrated in the separated disperse carbide.



**Fig. 4.14** Electronic image of the microstructure of the alloy 34NFM after quenching from 1250 °C in water and heating at 700 °C and the distribution pattern of the elements

According to the quantitative analysis the curve of the frequency density distribution of the sizes of carbide particles after heating at 700 °C alloy samples 34NFM was built, pre-quenched from 1250 °C in water (Figure 4.15). Analyzing the nature of the distribution it can be argued that the relative number of large particles after heating hardened samples hasn't changed. The height of the peak characterizing disperse particles, increased, and it displaced to the left in the region of lower values of the average area of 0.4-0.5  $\mu\text{m}^2$ . It speaks to the active selection of disperse inclusions from saturated solid solution during heating.

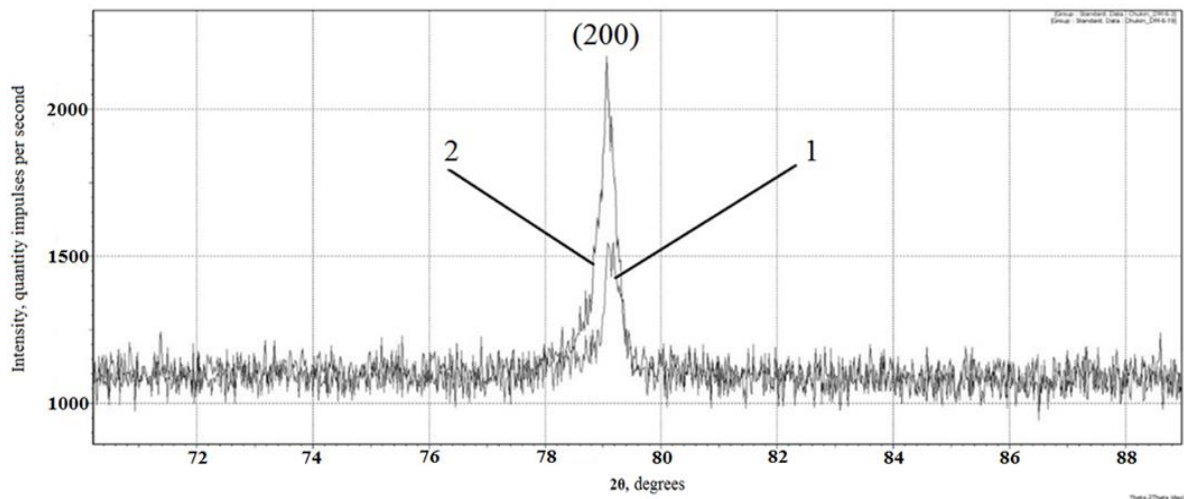


**Fig. 4.15** Distribution of particle sizes of carbides in the microstructure of the alloy 34NFM after quenching and after heating to 700 °C

Thus, we can conclude that heating is pre-quenched alloy 34NFM in the temperature range from 300 to 700 °C as the alloy 32NF the processes of aging is going, accompanied by increasing hardness in the result of the disperse hardening with the isolation mainly of vanadium carbides. X-ray diffraction analysis (Appendix 9) showed that the microstructure consists primarily of carbides of the type VC ( $\text{V}_4\text{C}_3$ ), and in some cases are complex carbides of molybdenum, vanadium and titanium. We can note that the

average size of precipitated carbides dispersed in the alloy 34NFM more than in the alloy 32NF, and their relative number is slightly less. This, obviously, is the reason for the smaller effect of disperse hardening alloy 34NF compares with the alloy 32NF.

Transcription of diffraction patterns obtained by single crystal XRD confirmed that the metal base is a  $\gamma$ -solid solution with the FCC lattice (Appendix 9). As in the case of the alloy 32NF, after aging the quenched alloy samples 34NFM a moving in the characteristic maximum of the reflection that is observed in the overlay of diffraction patterns from chilled and aged samples (Figure 4.16), and also the calculated lattice parameter has changed (Appendix 4). This indicates a change in alloyed  $\gamma$ -solid solution during aging as a result of the transition of carbon atoms and carbide-stabilizing elements in the carbide phase.



**Fig. 4.16** Characteristic peaks (200) for the quenched sample (1) alloy 34NFM and sample after aging at 700 °C (2)

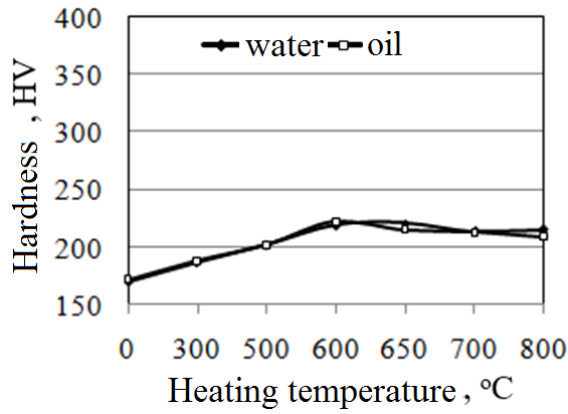
Maximum hardness when heated, alloy 34NFM was about 100 HV, and ultimate tensile strength - 450 N/mm<sup>2</sup> lower than in the alloy 32NF. This can

be explained by the fact that molybdenum were determined after quenching is present mainly in the indissoluble during heating for hardening of large carbides. Therefore, the  $\gamma$ -solid solution is slightly saturated with molybdenum (in contrast to vanadium). For this reason, the dispersed carbide particles emitted during heating of quenched alloy samples 34NFM, molybdenum is practically not observed. Thus, the additional alloying with molybdenum while reducing the content of carbon and vanadium were found to be less effective for dispersion hardening compared to 32NF alloy, doped only with vanadium.

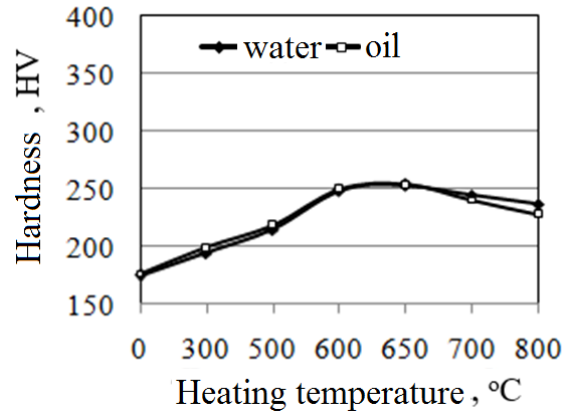
#### **4.5 The researches of the microstructure and mechanical properties after aging alloy 32NFK and discussion**

The results of hardness testing after heating the samples of the alloy 32NFK, previously quenched from 1200 and 1250 °C in water and in oil (Figure 4.17) showed that increasing the temperature of heating of quenched alloys from 300 to 650 °C is accompanied by increase of hardness. The largest hardness and ultimate strength are achieved by heating and aging at 650 °C. Hardness after aging of the alloy 32NFK quenched with 1250 °C was about 50 HV, while the strength was more on about 100 N/mm<sup>2</sup> in comparison with the properties of the samples quenched with a lower temperature of 1200 °C. The quenching medium had no effect on hardness with further heating.

Microstructure of the alloy 32NFK after heat treatment for maximum hardness is shown in Figure 4.18. It is a metal basis grain of different sizes with large and disperse particles. Quenching from higher temperatures leads to grain growth and reduction in the number of particles, and the cooling medium hasn't a strong influence on the nature of the structure. Results showed by SEM (Figure 4.19) that the number of disperse particles increases with increasing temperature from 300 to 650 °C.

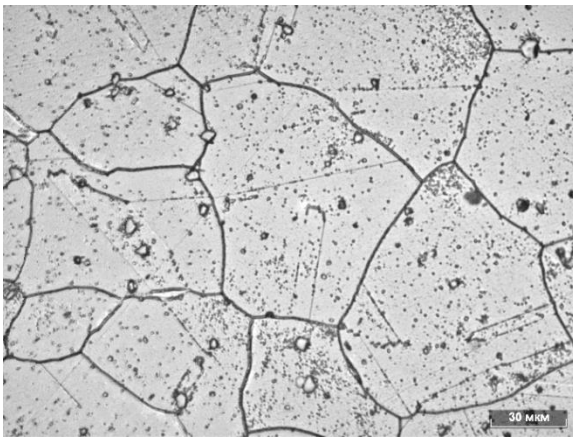


a

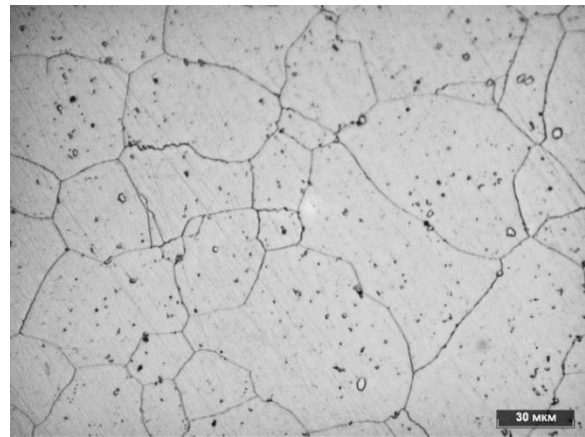


b

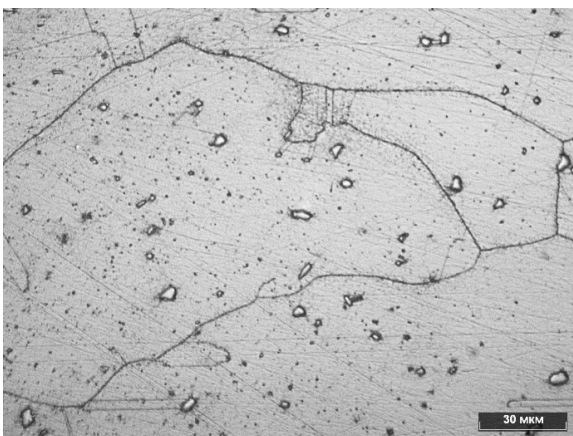
**Fig. 4.17** Change of hardness on heating 32NFK alloy pre-quenched from 1200 °C (a) and 1250°C (b)



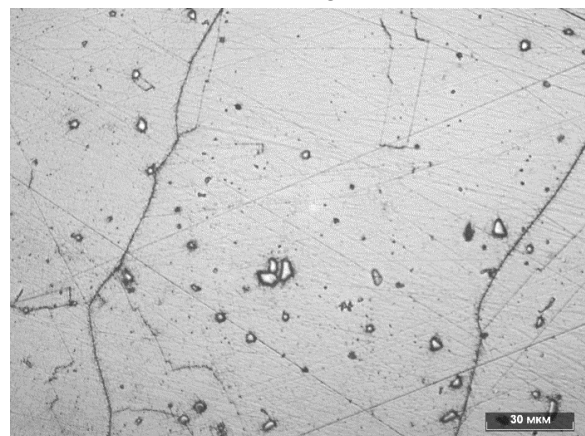
a



b



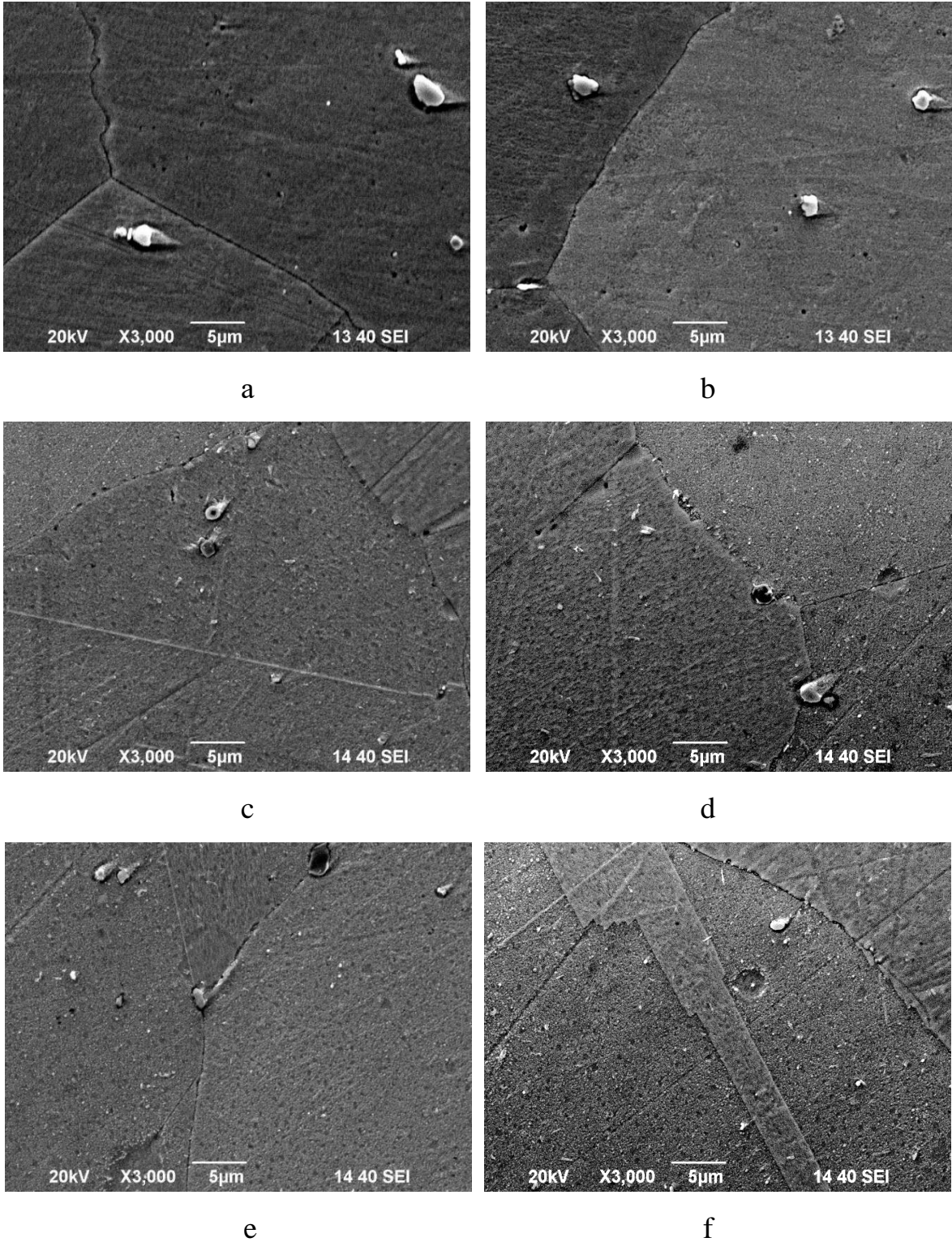
c



d

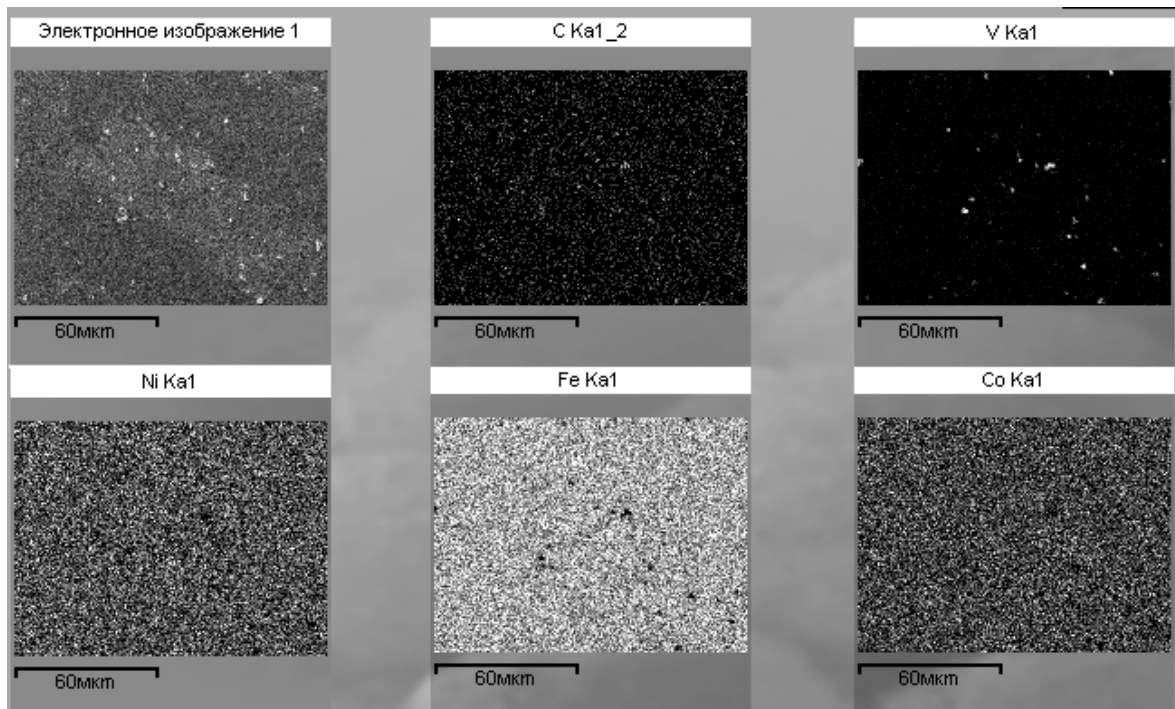
**Fig. 4.18** Microstructure of the alloy 34NFM after aging at 700 °C of samples quenched from 1200 °C (a, b) and 1250 °C (c, d) in water and oil (a, c) and in oil (b, d), x 500





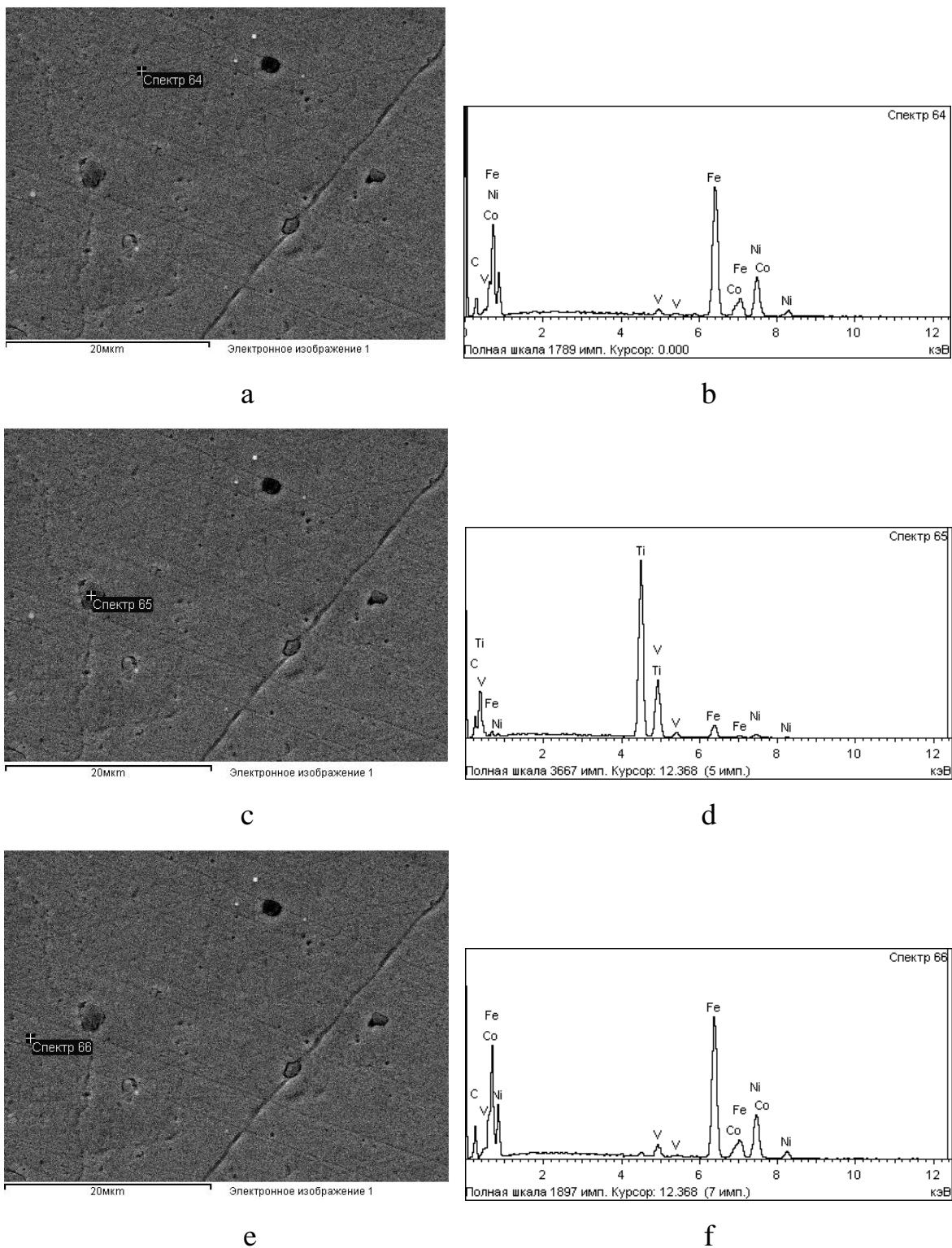
**Fig. 4.19** Electron microscopic image of the alloy 32NFK microstructure after quenching from 1200 °C (a, c, e) and 1250 °C (b, d, f) in water and aging at 300 °C (a, b), 600 °C (c, d) and 700 °C (e, f)

Maps of elements distribution (Figure 4.20) and the analysis of X-ray spectra (Figure 4.21) showed that the particles observing in the alloy 32NFK structure are carbides of vanadium, which formula PCA can be described as VC ( $V_4C_3$ ). As in alloys 32NF and 34NFK there are some titan in the large carbides, and the most disperse carbide particles don't contain it, that is an indirect proof of their isolation in the heating process, since the presence of titanium in these particles is due to the deoxidation of the alloy during melting. MRSA showed that in the spectra obtained from the metal base, the detected peaks of iron, nickel, cobalt, carbon, and vanadium (Figure 4.21, b).



**Fig. 4.20** Electronic image of the alloy 32NFK microstructure after quenching from 1250 ° C in water and heating at 650 ° C and the distribution pattern of the elements

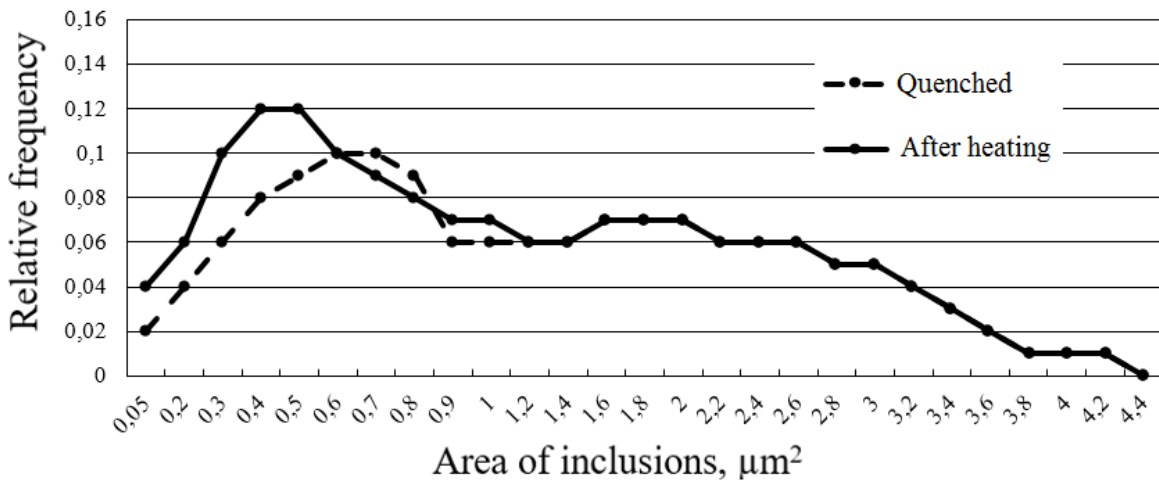
On the basis of a quantitative analysis of the structure the curve of the frequency density distribution of the sizes of carbide particles after heating



**Fig. 4.21** Electronic image of the alloy 32NFK microstructure (a, c, e) after quenching from 1250 ° C in water and heating at 650 c and typical characteristic spectra from metallic substrates (b) large particles (d) and fine particles (f), the carbide phase



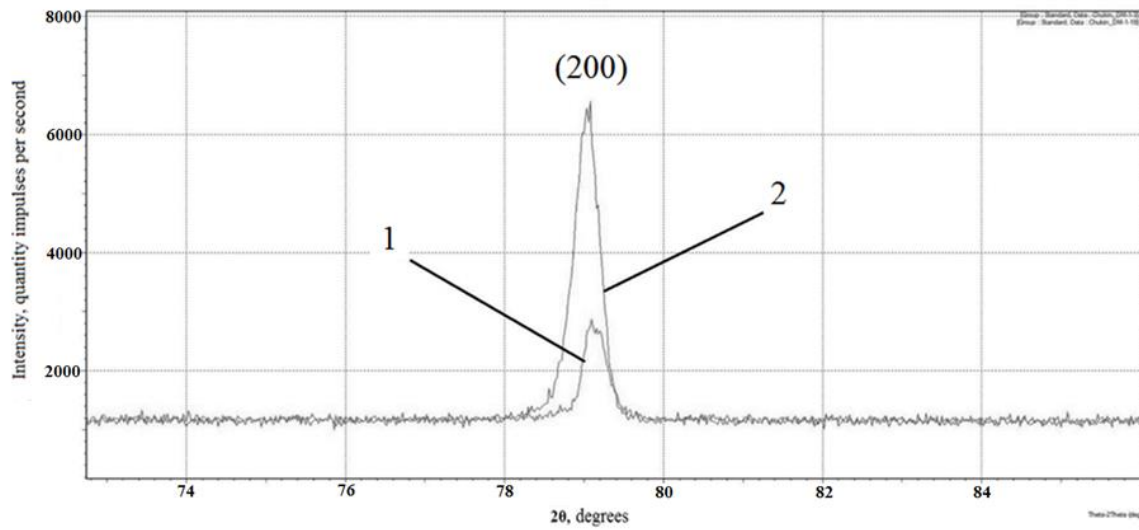
was built by heating to 650 °C of the alloy samples 32NFK, pre-quenched from 1250 °C in water (Figure 4.22). The distribution pattern shows that the relative number of large particles after heating quenched samples hasn't changed. The height of the peak characterizing the disperse particles increased slightly, and it displaced to the left in the region an average area of 0.4-0.5  $\mu\text{m}^2$ , indicating that the selection of disperse inclusions from saturated solid solution during heating. Thus, we can conclude that heating is the pre-quenched alloy 32NFK in the temperature range from 300 to 650 °C, as in alloys 32NF and 34NFM, the processes of aging are observed accompanying by increasing hardness as a result of the dispersion hardening with the isolation of vanadium carbides. However, it should be noted that in comparison with the alloys 32NF and 34NFM the number of precipitated carbide particles are much smaller. These data correlate well with the hardness values.



**Fig. 4.22** Distribution of the second phase particles sizes of the quenched sample and the sample after aging of the alloy 32NFK

By a single crystal XRD, it was confirmed that the metal basis is a  $\gamma$ -solid solution with the FCC lattice (Appendix 10). As in the case with the alloys

32NF and 34NFM, after aging the quenched alloy samples 32NFK the reflection characteristic maximum moving is observed, that is seen in the overlay of diffraction patterns from chilled and aged samples (Figure 4.23), and also changed the calculated lattice parameter (Appendix 4). This indicates a change in  $\gamma$ -solid solution alloying during aging as a result of carbon atoms transition and vanadium carbide in the isolating phase.



**Fig. 4.23** Characteristic peaks (200) for the quenched the alloy 32NFK sample (1) and the sample after aging at 650 °C (2)

Hardness, ultimate strength and yield strength of the alloy 32NFK was significantly lower than in the alloys 32NF and 34NFM and amounted to 250 HV, 800 N/mm<sup>2</sup>, 720 N/mm<sup>2</sup>, respectively. At the same time the increasing of quenched state hardness was also less significant in comparison with alloys 32NF and 34NFM and amounted to no more than 75 HV. Thus in the alloy 32NFK the lowest hardness among the investigated alloys is performed, which is attributed to the lower content of carbon (in comparison with the alloy 32NF) and carbide-stabilizing elements (in comparison with the alloy 34NFM).

## Conclusions Chapter 4

1. It is established that during aging of the alloys quenched in a supersaturated solid solution in the temperature range from 300 to 650-700 °C there is a disintegration of solid solution and the isolating mainly vanadium carbides, which formula can be described as VC ( $V_4C_3$ ), accompanying by increasing hardness, which indicates the disperse hardening.
2. Found that the number of disperse particles separated during aging in all the investigating alloys, pre-quenched from a higher temperature of 1250 °C, more than in the alloys, pre-quenched from 1200 °C, and a cooling medium used for quenching, hasn't a significant effect on the structure and mechanical properties after aging.
3. It is shown that the largest hardening in the alloys 34NFM (hardness 300 HV, the ultimate tensile strength = 870 N/mm<sup>2</sup>, yield strength = 780 N/mm<sup>2</sup>) and 32NF (hardness 400 HV, the ultimate tensile strength = 1150 N/mm<sup>2</sup>, yield strength = 1030 N/mm<sup>2</sup>) is achieved by quenching with a temperature of 1250 °C in water followed by aging at 700 °C. The largest hardening for the alloy 32NFK (hardness 250 HV, the ultimate tensile strength = 800 N/mm<sup>2</sup>, yield stress = 720 N/mm<sup>2</sup>) is implemented with the quenching with temperature 1250 °C in water followed by aging at 650 °C.
4. The obtained values of hardness and strength for the alloys 32NF, 34NFM and 32NFK correspond to TU 096652-123-91527977-15, so the models of thermal effect can be recommended as a hardening treatment for high-strength invar alloys manufactured in conditions of "Motovilikhinskiye Plants".

# **CHAPTER 5**

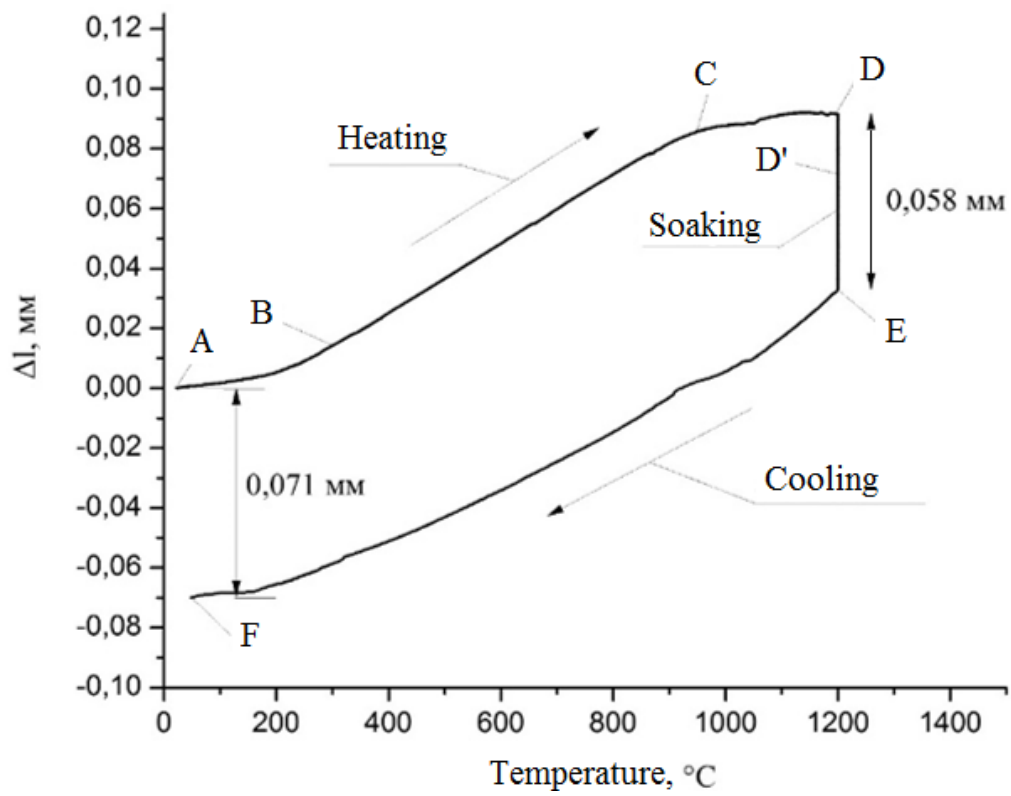
## **FEATURES OF THERMAL EXPANSION OF HIGH-STRENGTH INVAR ALLOYS**

### **5.1 Results of the dilatometric Invar alloys study during quenching**

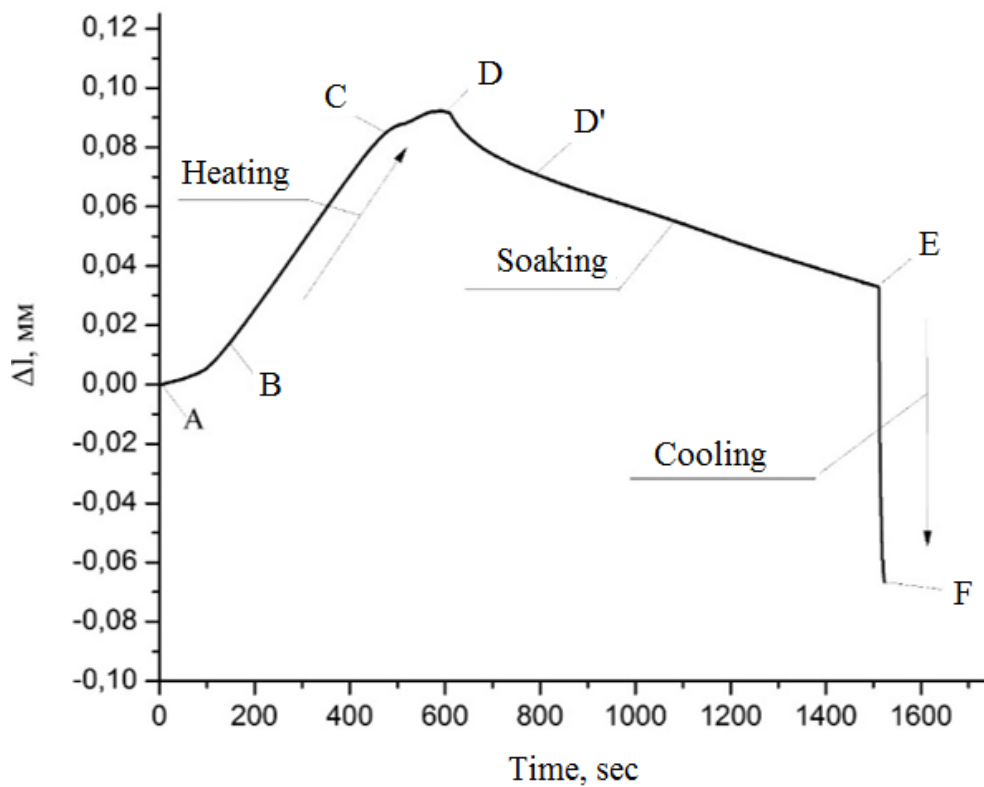
Physical modeling of heat treatment regimes, as well as experiments to determine the coefficient of linear thermal expansion (CTE) were carried out on Gleeble complex 3500.

As described in Chapter 4, the alloy 32NF showed the highest hardening by quenching and subsequent aging. The dilatometric curves shown in Figure 5.1, give an idea of the changes in linear dimensions ( $\Delta l$ ) of the sample depending on the temperature (Figure 5.1 a) and time (Figure 5.1, b) of the thermal effect in quenching of the alloy 32NF. Dilatometric diagrams shown in Figure 5.1, illustrate the change of the sample size of the Invar alloy 32NF during heating for quenching to 1200 °C, its holding at this temperature, and accelerated controlled cooling simulating cooling in water.

Heating to the temperature of 1200 °C was taking place for 10 minutes and was accompanied by an increase in linear dimensions of the entire time interval. In the range from the room temperature to 300 °C, the curve is not linear (Figure 5.1, section AB) due to the manifestations of the Invar effect i.e. magnetostriction. In the temperature range from 300 to 950 °C the heat dilatometric curve is linear (Figure 5.1, section BC) that represents the thermal expansion (increase of linear size), without occurrence of any structural phase transformations. In the temperature range from 950 to 1200 °C, the curve changes the tilt angle (Figure 5.1 a, section CD). All the above stated indicates a slowing of thermal expansion that is associated with the development of the process of dissolution of the carbide phase in the specified temperature range.



a



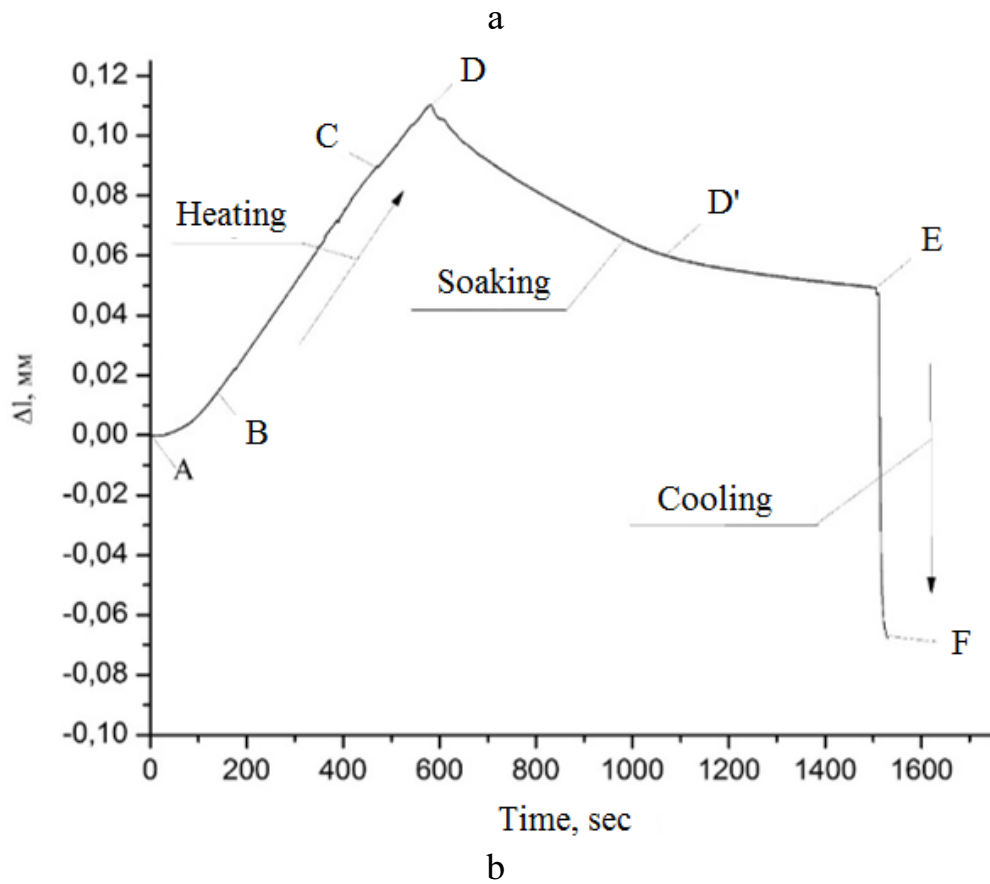
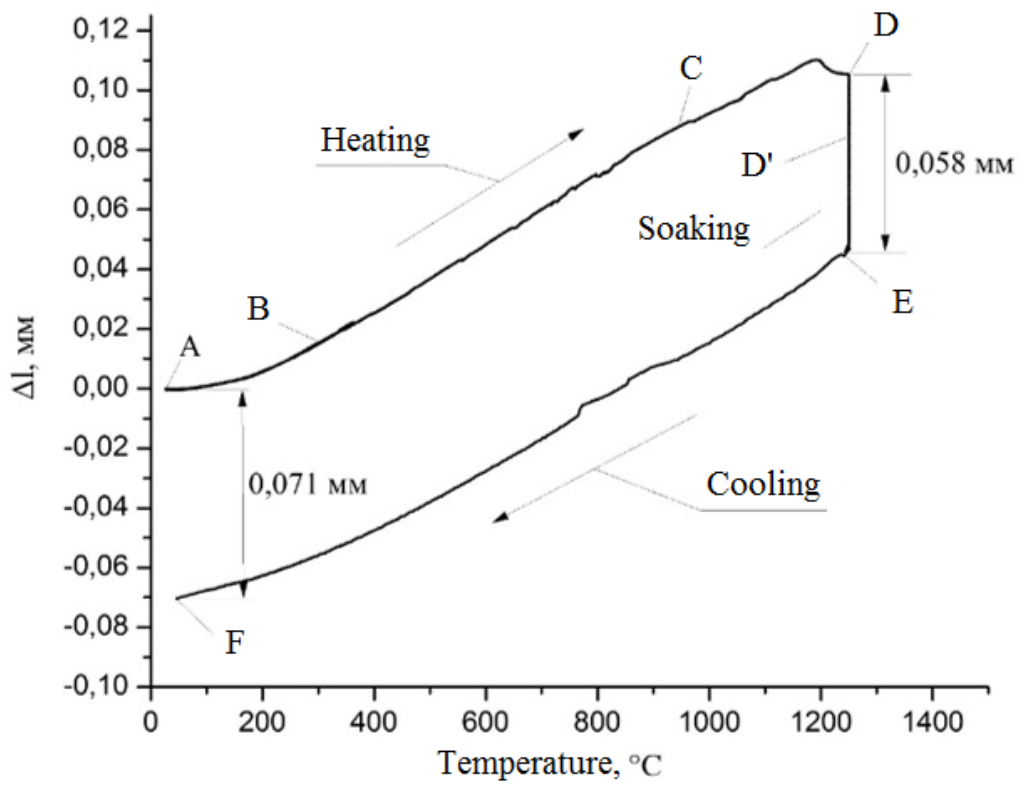
b

**Fig. 5.1** Dilatometric quenching from 1200  $^{\circ}\text{C}$  in the alloy in water 32NF coordinates ( $\Delta l$ ) - temperature (a) and ( $\Delta l$ ) - time (b)

Further isothermal holding at 1200 ° C during 15 minutes (Figure 5.1 the section DE) leads to a reduction of linear dimensions at 0.058 mm. Such significant narrowing at a constant temperature indicates the intense dissolution of carbides, accompanied by homogenization of the austenite. In the initial period of aging for about three minutes (Figure 5.1, section DD') the slope of the curve is more than in the section D'E obviously because of the greater dissolution rate of the carbide phase in the initial exposure period.

The following rapid cooling, simulating quenching in water, captures gamma-solid solution without the occurrence of phase transitions and, as expected, is characterized by a sharp decrease in linear dimensions due to thermal contraction (see Figure 5.1, section EF). So after hardening simulation from 1200 °C in water the absolute sizes of the test sample reduced by 0.071 mm.

The size changing of the sample during hardening of the alloy 32NF from the temperature 1250 ° C is shown in Figure 5.2. The nature of the curve is substantially similar to dilatometric curves obtained when tempering from 1200 °C, but differs in that there is no pronounced section of deceleration of the thermal expansion on the curve upon heating to the quenching temperature (1250 °C), and the deflection on the curve during isothermal aging at this temperature (Figure 5.2, CD section) is greater compared with the exposure at the temperature of 1200 ° C. This is due to the higher temperature of heating and thus a higher rate of dissolution of the carbide phase. Thus, as the structural studies performed [110] showed a more complete dissolution of the carbides takes place, resulting in reduced coefficient of linear expansion compared to quenching from 1200 °C. In such a way there is a more complete saturation of the solid solution with carbon and alloying elements, which upon the subsequent heating of the quenched samples should improve the hardness by age hardening in a release of vanadium carbides.



**Fig. 5.2** Dilatometric quenching from 1250  $^{\circ}\text{C}$  in water in the coordinates alloy 32NF ( $\Delta l$ ) - temperature (a) and ( $\Delta l$ ) - time (b)

The dependences of the linear dimensions from time in determining the CTE of the alloy 32NF, tempered from 1200 and 1250 °C are shown in Figure 5.3. According to the method of determining the CTE in accordance with GOST 14080-78 the values of relative elongation were obtained: after quenching from 1200 °C  $\Delta l = 0.00231$  mm, after hardening from 1250 °C  $\Delta l = 0.00218$  mm. The calculated values of the CTE in a temperature range of 20-150 °C were as follows: after quenching from 1200 °C  $\alpha_{20-150} = 1.93 \times 10^{-6} \text{K}^{-1}$ , after hardening from 1250 °C  $\alpha_{20-150} = 1.82 \times 10^{-6} \text{K}^{-1}$ .

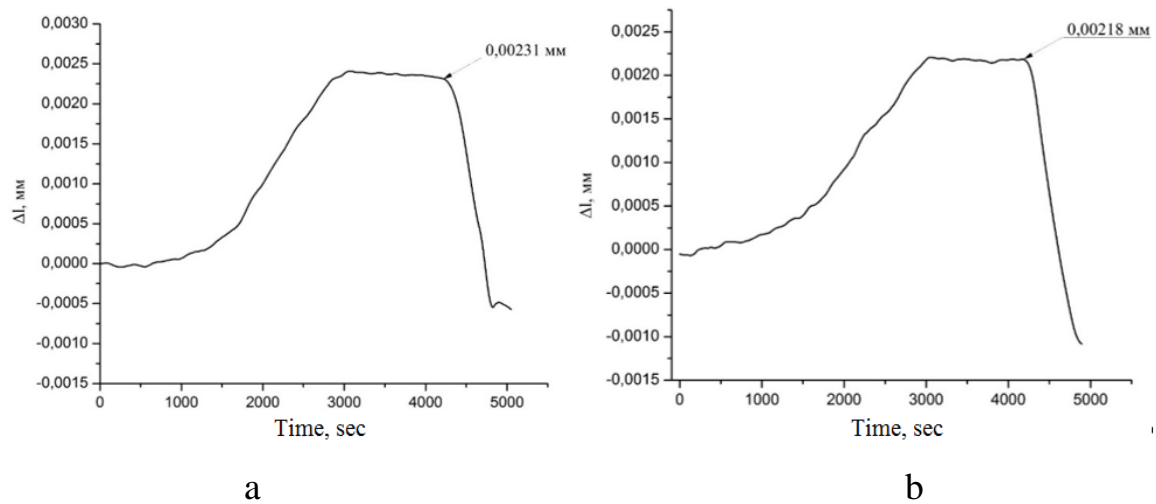


Fig. 5.3 Dilatometric curve, taken during the test the CTE of the 32NF alloy, tempered from 1200 (a) and 1250 °C (b)

When heating for quenching to 1250 °C, as shown by structural studies performed (see chap. 3), as compared to heating up to 1200 °C a complete dissolution of the carbides and the saturation of the solid solution by alloying elements takes place. This reduces the value of the CTE ( $\alpha_{20-150} = 1.82 \times 10^{-6} \text{K}^{-1}$ ) and is accompanied by an increase in hardness during the subsequent aging (see chap. 4).

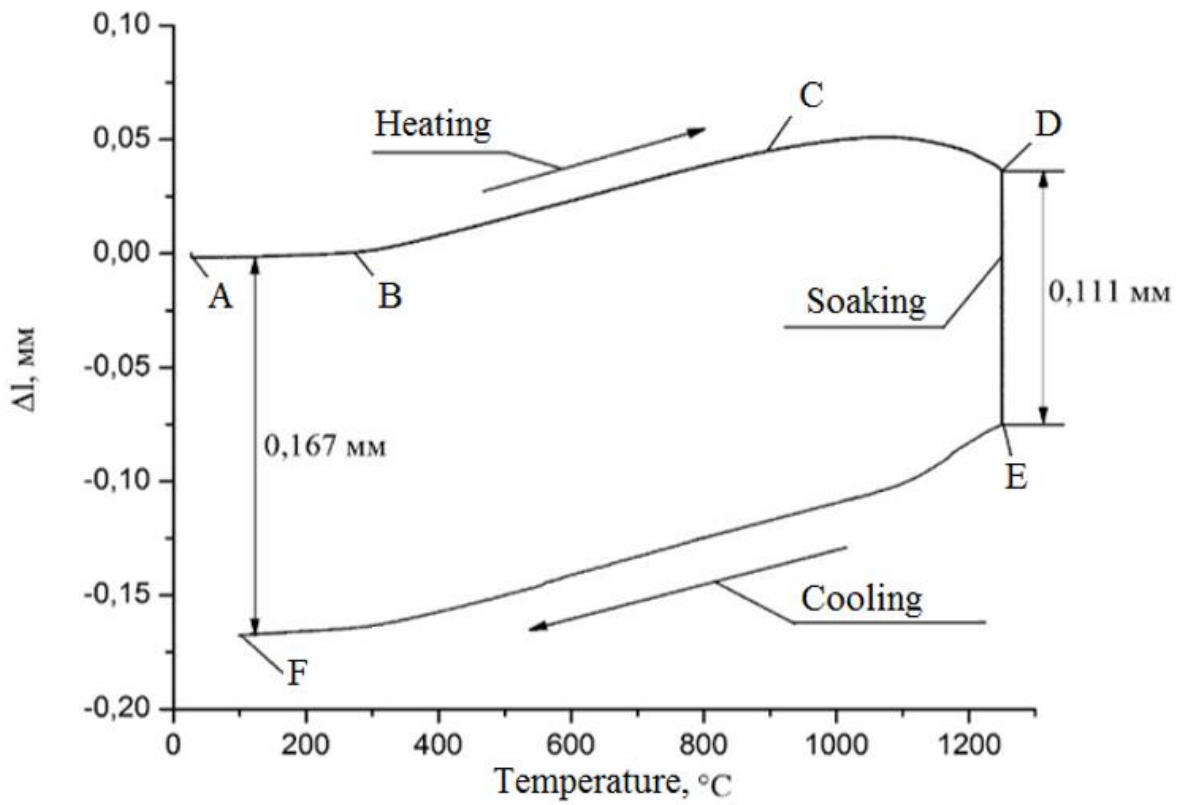


Similar dilatometric investigations were carried out for the alloy 34NFM. The character of dilatometric curves appeared to be identical to the curves obtained for the alloy 32NF, and differed only in quantitative values of  $\Delta l$ . After quenching of the alloy 34NFM from 1200 °C the relative elongation value calculated by dilatometric curves was  $\Delta l = 0.00304$  mm and the value of the CTE was  $\alpha_{20-150} = 2.53 \times 10^{-6}\text{K}^{-1}$ , and after hardening from 1250 °C -  $\Delta l = 0.00292$  mm,  $\alpha_{20-150} = 2.43 \times 10^{-6}\text{K}^{-1}$ .

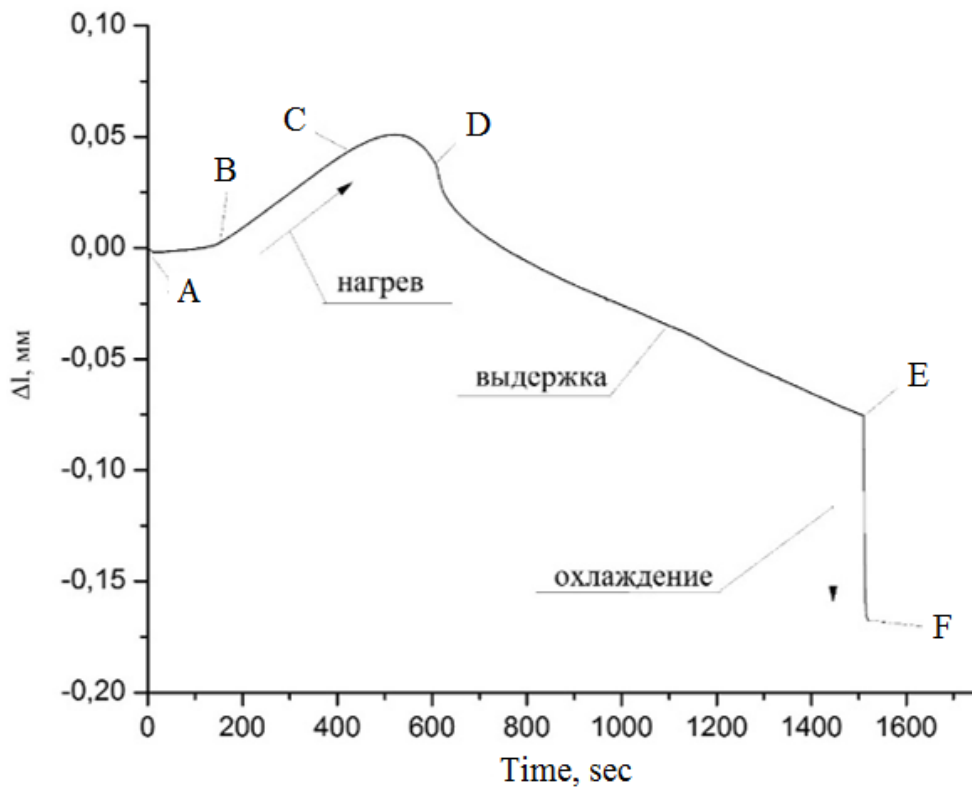
Dilatometric diagrams shown in Figure 5.4, illustrate the change of sample sizes of the Invar alloy 32NFK during heating for quenching up to 1250 °C, its holding at this temperature and accelerated controlled cooling simulating cooling in water.

The character of dilatometric curve is identical to the obtained ones on alloys 32NF and 34NFM on equal treatment hardening regimes, but the absolute value of the change in linear dimensions after heating up to 1250 °C (Figure 5.4, a, point D) is less than for the alloys 32NF and 34NFM: 0.036 mm for 32NFK, 0.98 mm for 34NFM and 0.105 mm for 32NF. This is due to the influence of cobalt, which restrains the thermal expansion by doping the solid solution [68, 74, 75, 85, 94]. Also it is worth noting that at the isothermal holding at 1250 °C, the reduction of the sample was 0.111 mm, which is almost twice more than the reduction of the 32NF at the same exposure.

After quenching of the alloy 32NFK from 1200 °C, the value of the relative lengthening calculated from dilatometric curves is  $\Delta l = 0.00142$  mm, and the value of the CTE is  $\alpha_{20-150} = 1.18 \times 10^{-6}\text{K}^{-1}$ , and after hardening from 1250 °C  $\Delta l = 0.00109$  mm,  $\alpha_{20-150} = 0.91 \times 10^{-6}\text{K}^{-1}$ . It is worth noting that after quenching the values of the CTE correspond to the technical requirements, but the mechanical properties do not meet them (see chap. 3).



a



b

**Fig. 5.4** Dilatometric quenching from 1250  $^{\circ}\text{C}$  in water in the alloy 32NFK coordinates ( $\Delta l$ ) - temperature (a) and ( $\Delta l$ ) - time (b)

## 5.2 The results of the dilatometric study of the Invar alloys during aging

For the alloys 32NF and 34NFM, as shown by previous studies, the highest values of hardness and ultimate strength were obtained by aging at 700 °C for 1 hour and when the alloy 32NFK is exposed at 650 °C for 1 hour (see chap. 4), therefore the study of the thermal expansion and determination of CTE were carried out on samples treated according to these modes. In the results analysis of the dilatometric studies of the competing processes: the depletion of solid solution by carbon atoms, which should lead to reduction of the specific volume and the precipitation of carbides, which causes an increase in volume.

In Figure 5.5, the dilatometer curve shows a change in linear dimensions when heated and held isothermally for 1 hour at 700 °C of the alloy sample 32NF quenched from 1250 °C temperature. A detailed examination of the dilatometric curve during the isothermal holding an increase in the linear dimensions (Figure 5.5, b, section AB) that can be attributed to the release of the carbide phase from a supersaturated solid solution fixed by hardening.

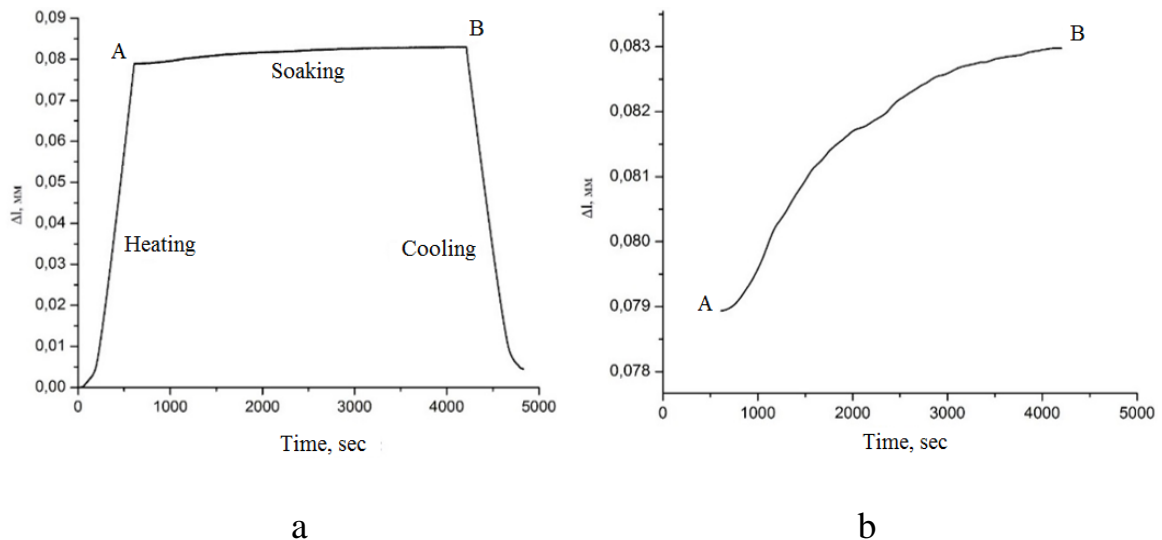
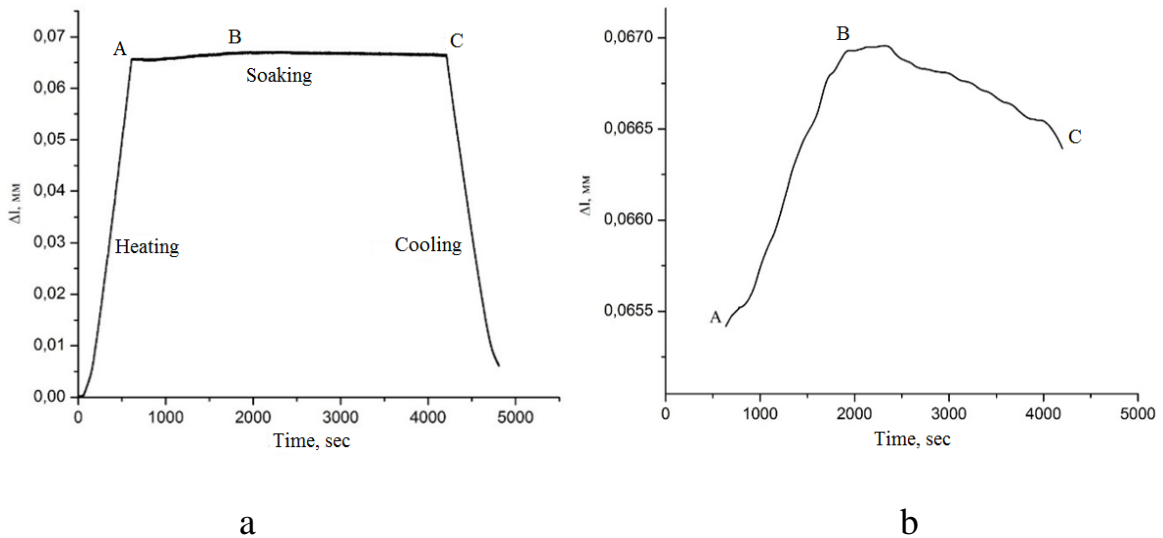


Fig. 5.5 Dilatometric aging at 700 °C for 1 h 32NF alloy pre-hardened from 1250 °C (a) and dilatometric curve plot of isothermal holding in the range (b)

General view of the dilatometric heating and isothermal holding curve at 700 °C alloy 34NFM sample, pre-hardened from 1250 °C, presented in Figure 5.6, a does not differ from similar dilatometric curves for the alloy 32NF, but two areas can be distinguished by detailed consideration during the isothermal holding (Figure 5.6, b). At the beginning of the isothermal soaking (Figure 5.6, b, section AB) an increase in the linear dimensions is seen on the curve, that is also due to the release of the carbide phase, from a supersaturated solid solution fixed by hardening. But in 1800 sec of exposure an increase in the linear dimensions begins to decelerate, indicating a slowing down of the process of the carbide phase separation. By increasing the exposure time of more than 1900 sec a decrease in the size of the sample is recorded (Figure 5.6, b, section BC) due to the coagulation of precipitated carbide particles.

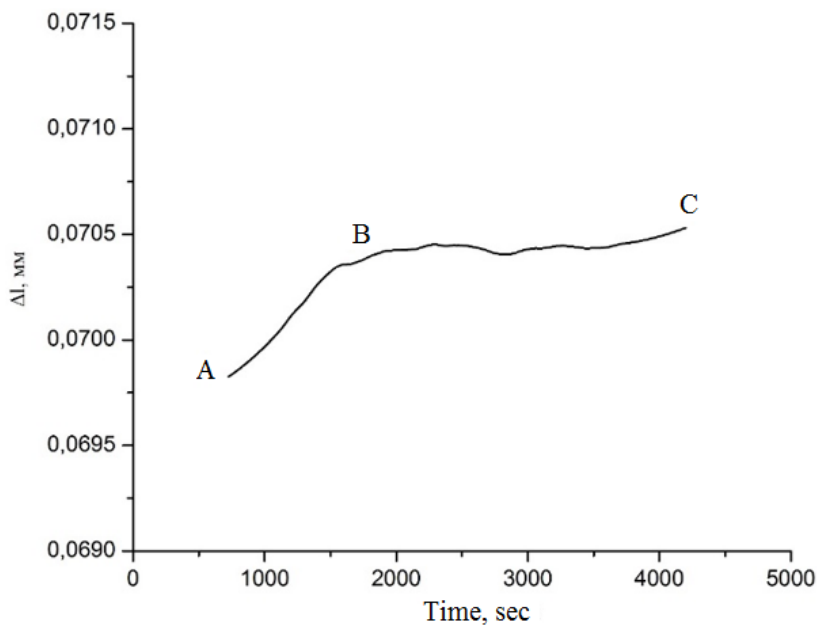


**Fig. 5.6** Dilatometric aging at 700 ° C for 1 h 34NFM alloy pre-hardened from 1250 °C (a) and dilatometric curve section in the range of isothermal soaking (b)

The alloy 34NFM unlike the alloys 32NFK and 32NF in the composition of carbides along with vanadium molybdenum is present which is a weaker

carbide forming element that causes coagulation of the carbide phase during the isothermal holding at 700 °C. This is supported by structural studies (see chap. 4), in which it was found that the average size of carbide particles after aging at 700 °C in the alloy 34NFM was 0.45  $\mu\text{m}^2$  and was larger than the average area of the carbide particles in the alloy 32NF (0.25  $\mu\text{m}^2$ ).

Figure 5.7 shows the change in linear dimensions during isothermal holding at 650 °C the alloy sample 32NFK quenched from 1250 °C. An active decomposition of the supersaturated solid solution with the release of vanadium carbides, accompanied by an increase in the linear dimensions (Figure 5.7, AB section) takes place since the beginning of the isothermal holding for 15 minutes.

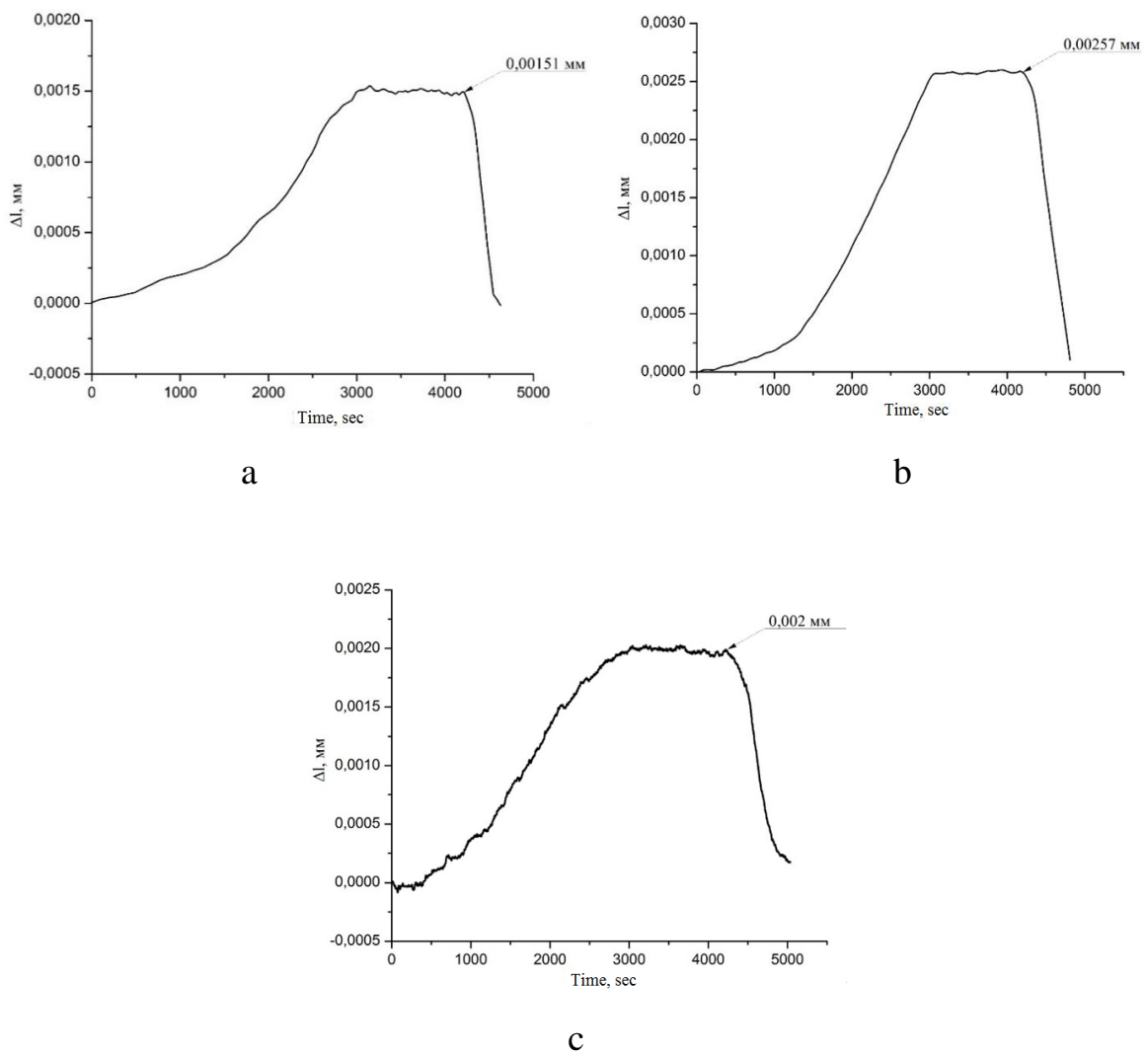


**Fig. 5.7** The dilatometric curve section in the range of the isothermal holding while aging at 650 °C for 1 h the alloy 32NFK previously hardened from 1250 °C

With further isothermal holding of the alloy 32NFK almost a horizontal section (Figure 5.7, section BC) is observed on the dilatometric curve, in contrast to

the dilatometric curve of the alloy 32NF (see. Figure 5.5, b), where there is no such section. This indicates a decrease in activity of the carbide phase separation, due to the presence of cobalt in the alloy 32NFK which, being in a solid solution increases its resistance to decay.

The dependences of the linear dimensions from time in determining the CTE of the alloys 32NF, 34NFM and 32NFK after aging according to the regimes mentioned above, providing a maximum hardness are shown in Figure 5.8.



**Fig. 5.8** Dilatometric curves taken during the CTE test of the alloys 32NF (a) and 34NFM (b) after aging at 700 °C and of the alloy 32NFK (c) after aging at 650 °C

The values of the relative elongation when heated were determined from the obtained data, which are as follows: 0.00151 mm for the alloy 32NF, 0.00257 mm for the alloy 34NFM and 0.002 mm for the alloy 32NFK. The calculated values of CTE are as follows: for the alloy 32NF  $\alpha_{20-150} = 1.26 \times 10^{-6}K^{-1}$ , for the alloy 34NFM  $\alpha_{20-150} = 2.14 \times 10^{-6}K^{-1}$ , and for the alloy 32NFK  $\alpha_{20-150} = 1.67 \times 10^{-6}K^{-1}$ . The CTE test results after various heat treatment conditions are shown in Table 5.1.

**Table 5.1** Results of tests to determine the value of the CTE after various heat treatment regimes investigated alloys

Alloy grade	Heat treatment regimes	CTE value $\alpha_{20-150}, \times 10^{-6}K^{-1}$
32NF	Hardening from 1200 °C in water	1.93
	Hardening from 1250 °C in water	1.82
	Hardening from 1250 °C in water, followed by heating to 700 °C with soaking for 1 h	1.26
34NFM	Hardening from 1200 °C in water	2.53
	Hardening from 1250 °C in water	2.43
	Hardening from 1250 °C in water, followed by heating to 700 °C with soaking for 1 h	2.14
32NFK	Hardening from 1200 °C in water	1.18
	Hardening from 1250 °C in water	0.91
	Hardening from 1250 °C in water, followed by heating to 700 °C with soaking for 1 h	1.67

### **5.3 Influence of the stabilizing heat treatment**

As noted in Chapter 1, the dimensional stability is one of the most important characteristics of the Invar alloy. In this regard, investigations were conducted on the effect of heating on the stability of the absolute size of Invars samples. For this samples of the alloys 32NF 34NFM and 32NFK pretreated by modes, providing maximum values of strength properties and minimum values of the CTE, have been heated to a temperature of 150 °C (corresponding to technical requirements of the maximum operating temperature) with holding for 20 minutes and the following slow cooling. Dilatometric curves taken during the experiments presented in Figure 5.9, show that after cooling to room temperature, the absolute sizes of the samples decreased by 0.002175 mm for the alloy 32NF, by 0.001842 mm for the alloy 34NFM and by 0.002494 mm for 32NFK alloy.

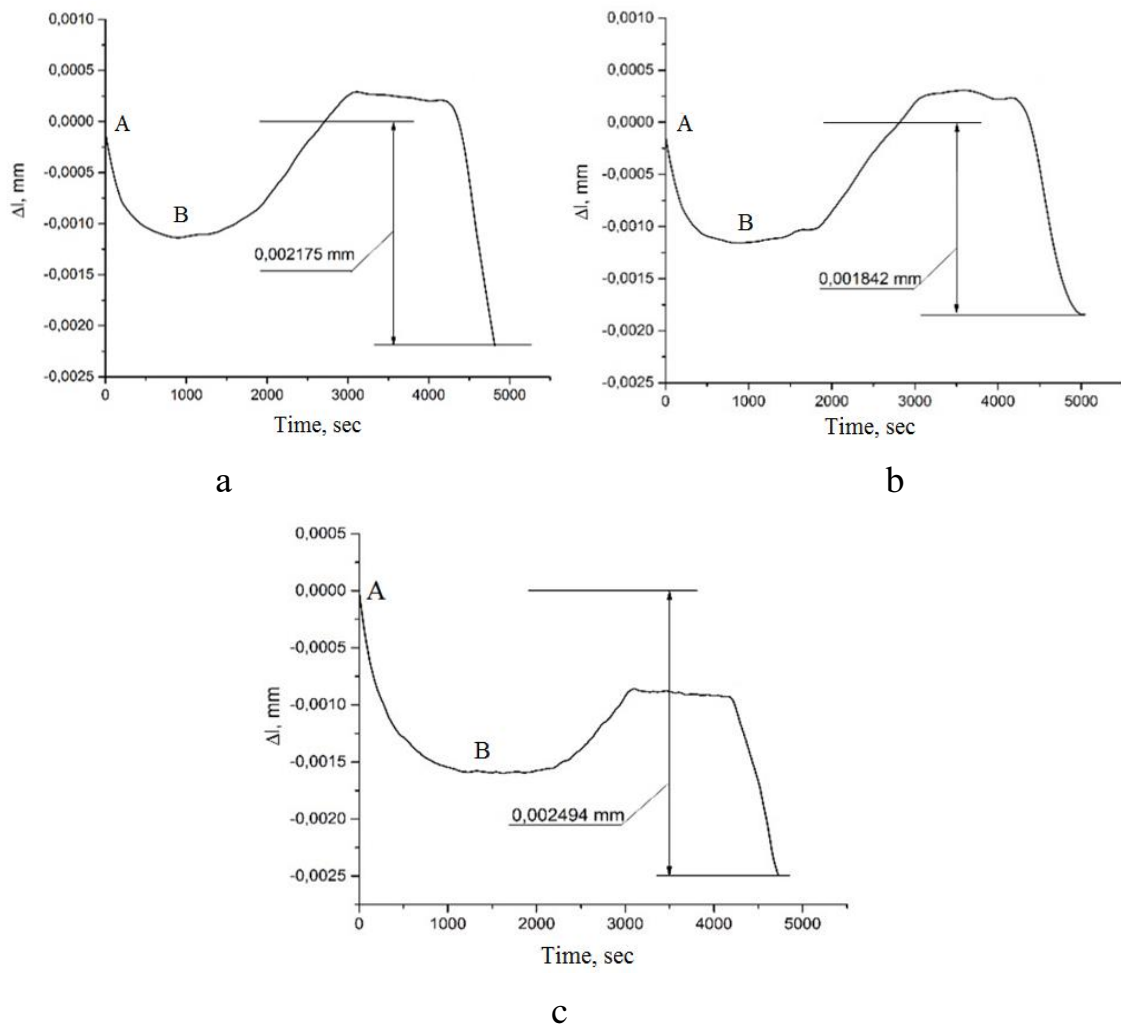
Special attention is drawn to an abnormal reduction in the sample sizes, fixed during heating from room temperature to 65 °C (section AB in Figures 5.10, a, b, c). There are papers in the scientific literature proving the existence of this effect [34, 42, 64, 74], in which this anomaly is explained by the predominance of magnetostrictive effects in the crystal lattice of the austenite over the thermal expansion.

Thus after aging at high temperatures of 650-700 °C and a crystalline structure of high magnetic domain of the high - strength invar alloys based on the system Fe-Ni-C alloyed by cobalt, vanadium and molybdenum is in an unstable state that does not allow using the invar alloys studied, 32NF, 34NFM and 32NFK for the manufacture of precision engineering components at a temperature of 20-150 °C during the operation without additional stabilizing treatment.

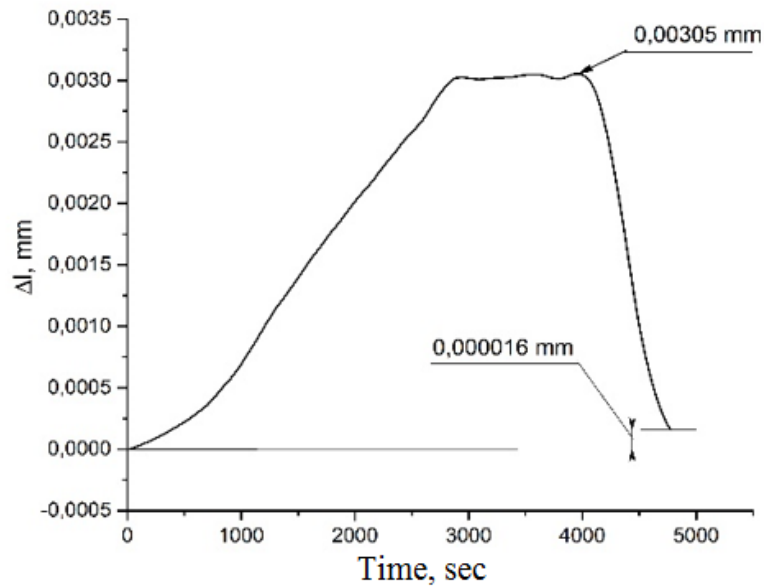
The stabilization treatment consisting in holding at 80 °C for 48 hours, was conducted on the samples of alloys 32NF, 34NFM and 32NFK pretreated by the mode shown in table 5.1: hardening from 1250 °C in water and aging at



650-700 °C for 1 hour. Dilatometric tests of the CTE of the alloy 32NF after stabilization are shown in Figure 5.10. It has a classic look, with no abnormal areas of narrowing in the entire temperature range. The value of the coefficient  $\alpha_{20-150} = 1.3 \times 10^{-6} K^{-1}$  and the change in the absolute size of the sample after a thermal cycle of tests are on two orders of magnitude smaller than without stabilization processing. Similarly, the values of coefficient of linear expansion were determined after stabilizing treatment of the alloys 34NFM and 32NFK (Table 5.2).



**Fig. 5.9** The dilatometric curves of additional heating at 150 °C of the alloys 32NF (a), 34NFM (b) and 32NFK (c) after quenching and aging on the regimes as specified in Table 5.1



**Fig. 5.10** Dilatometric curve, taken in the CTE test of the alloy 32NF sample treated according to the regime: quenching from 1250 °C, heating at 700 °C for 1 hour and stabilizing soaking at 80 °C for 48 hours

Thus, the study of the processes of linear dimensions change and definition of the CTE values showed that, for all modes of heat treatment, providing an increase in strength properties, the CTE preserves low values ( $\alpha \leq 3 \times 10^{-6} \text{ K}^{-1}$ ), which can be stabilized with additional special heat treatment i.e. the aging at 80 °C for 48 hours. This allows recommending the heat treatment regimes of the Invar alloys 32NF, 34NFM and 32NFK that provide their high strength, the minimum values of the CTE and dimensional stability in the operating temperature range of 20-150 °C, as shown in table 5.2. The tested alloys subjected to a hardening heat treatment, are superior, or at least not inferior in the properties to the closest foreign analogues.

The results of the dissertation research are used in the production sites of PJSC “Motovilikhinskiy plants“. Introduction of the developed measures makes possible to ensure the production of competitive products, which is confirmed by the act of implementation (Appendix 11).

**Table 5.2** Recommended modes of heat treatment and the resulting properties of the tested Invar alloys 32NF, 34NFM and 32NFK

Alloy grade	Heat treatment regimes	Свойства		
		Hardness, HV	UTS, N/mm <sup>2</sup>	CTE $\alpha \times 10^{-6}, K^{-1}$
32NF	Hardening from 1250 °C in water, followed by heating to 700 °C with soaking for 1 h, followed by heating to 80°C with soaking for 48 h	400	1150	1.3
34NFM	Hardening from 1250 °C in water, followed by heating to 700 °C with soaking for 1 h, followed by heating to 80°C with soaking for 48 h	300	870	2.18
32NFK	Hardening from 1250 °C in water, followed by heating to 650 °C with soaking for 1 h, followed by heating to 80°C with soaking for 48 h	250	800	1.7

### Conclusions on Chapter 5

1. Qualitative and quantitative dependences of the linear dimensions changes of the Invar alloys samples Fe-Ni-C, alloyed with vanadium, cobalt and molybdenum, on the temperature-time regimes of strengthening and stabilizing heat treatments.

2. It is shown that by heating for hardening of the studied alloys in the temperature range from 950 to 1200-1250 °C the dilatometric curve changes the slope, indicating slowing down of the thermal expansion due to the dissolution of the carbide phase. The subsequent holding at 1200-1250 °C leads to a sharp decrease in linear dimensions, indicating the intense dissolution of carbides, and the homogenization of the austenite.
3. It was revealed that while aging of quenched alloys in the range of isothermal holding at 650-700 °C for 1 hour, an increase of linear dimensions is observed, due to the release of the dispersed carbide phase from the supersaturated solid solution fixed by hardening.
4. Adaptation of the research complex functions Gleeble 3500 for the experiments on measuring the thermal coefficient of linear expansion in accordance with GOST 14080-78 has been conducted.
5. The values of the CTE after hardening heat treatment have been determined and found that for all the alloys the values of the CTE do not exceed  $\alpha_{20-150} = 3 \times 10^{-6} \text{K}^{-1}$  and conform to the requirements of TR 096652-123-91527977-15.
6. Instability of absolute linear dimensions and values of the CTE after the hardening heat treatment has been demonstrated. This instability is eliminated by the additional stabilizing thermal treatment consisting in holding at 80 °C for 48 hours.
7. The modes of strengthening and stabilizing heat treatments of the Invar alloys under study 32NF, 34NFM and 32NFK providing the necessary level of mechanical properties ( $\text{UTS} \geq 800 \text{ N/mm}^2$ , hardness 250 - 400 HV) and low values of the coefficient of linear expansion  $\alpha \leq 3 \times 10^{-6} \text{ K}^{-1}$  have been recommended (see table 5.2).
8. The obtained results are used in conditions of “Motovilikhinskiy plants” in the development of the technology of blanks production from high-strength

Invar alloys of a new generation, which are not inferior to world standards, as confirmed by an act of implementation (see. Appendix 11).

# CONCLUSIONS

Set and solved actual tasks to determine the regimes of heat treatment for improving the strength values while maintaining a low temperature coefficient of linear expansion of Invar alloy Fe-Ni-C system, alloyed with cobalt, vanadium and molybdenum. The main results reinforce the provisions of metal science related to theoretical and experimental studies of structural transformations in Invar alloys under various external effects, and are given below.

1. Reveal specific features of the structure of hot-rolled Invar alloys of the Fe-Ni-C-V, Fe-Ni-C-Co-V, Fe-Ni-C-V-Mo, showing that the major structural elements in them is gamma-solid solution with FCC, doped with cobalt, vanadium and molybdenum, carbides containing vanadium and / or molybdenum and non-metallic inclusions of metallurgical origin.
2. It was established that during heating for quenching alloys 32NF, 34NFM, 32NFK and a dissolution of the carbide phase (primarily molybdenum carbides) and the saturation of the solid solution carbon and carbide-forming elements: vanadium and molybdenum. However, to get a fully single-phase state of the alloy, even when heated to 1250 °C is not possible, and part carbides remains undissolved. In this case quenching from a higher temperature of 1250 °C dissolves greater number of inclusions compared to quenching from 1200 °C shown that upon heating for quenching observed noticeable grain growth, thus increasing the quenching temperature to 1250 °C is accompanied by a decrease of hardness
3. It was found that during the heating hardened alloys precipitation hardening mechanism is realized with isolation dispersed carbide particles,

preferably a vanadium carbides, the formula of which may be described as VC ( $V_4C_3$ ), increased strength properties. The number of dispersed carbide particles, isolated by heating, and strength characteristics in all investigated alloys previously hardened from a temperature higher 1250 °C, higher than the alloys previously hardened from 1200 °C.

4. It is shown that the largest hardening in the alloys 34NFM (hardness 300 HV, the ultimate tensile strength = 870 N/mm<sup>2</sup>, yield strength = 780 N/mm<sup>2</sup>) and 32NF (hardness 400 HV, the ultimate tensile strength = 1150 N/mm<sup>2</sup>, yield strength = 1030 N/mm<sup>2</sup>) is achieved by quenching with a temperature of 1250 °C in water followed by aging at 700 °C. The largest hardening for the alloy 32NFK (hardness 250 HV, the ultimate tensile strength = 800 N/mm<sup>2</sup>, yield stress = 720 N/mm<sup>2</sup>) is implemented with the quenching with temperature 1250 °C in water followed by aging at 650 °C. The values obtained for hardness and ultimate tensile strength of alloys 32NF, 34NFM, 32NFK and conform to the TR 096652-123-91527977-15, so these regimes of thermal treatment can be recommended as a reinforcing treatment for high-strength Invar alloys produced under conditions of "Motovilikhinskiy plants".

5. Established the regularities of the change in linear dimensions of samples of Invar alloys of the Fe-Ni-C, alloyed with vanadium, cobalt and molybdenum, on the temperature-time regimes hardening heat treatment. It is shown that by heating for hardening the alloys in the temperature range from 950 to 1200-1250 °C, the thermal expansion of a slowdown due to the dissolution of the carbide phase. The subsequent exposure at 1200-1250 °C leads to a sharp decrease in linear dimensions due to intensive dissolution of carbides, and the homogenization of the austenite. Upon heating the quenched alloy in the range of isothermal heating at 650-700 °C for 1 h, observed an increase of the linear dimensions cause separation of dispersed carbide phase

of the hardening fixed solid solution. Increasing the exposure time reduces the linear dimensions of the sample, due to the coagulation of the carbide phase.

6. Adapted functions of research complex Gleeble 3500 for experiments on measuring the thermal coefficient of linear expansion in accordance with GOST 14080-78. Determinate the values of the coefficient of linear expansion after various heat treatment regimes. It was found that for all values the alloys coefficient of linear expansion after hardening heat treatment does not exceed  $\alpha_{20-150} = 3 \times 10^{-6} \text{K}^{-1}$  and comply with TR.

7. Demonstrated instability absolute linear dimensions and values coefficient of linear expansion after hardening heat treatment, which eliminated the proposed additional stabilizing heat treatment consists of exposure at 80 °C for 48 hours.

8. Recommended for alloys 32NF, 34NFM, 32NFK heat treatment regimes used for the organization in the conditions of «Motovilikhinskiy plants» of small-tonnage production of blanks from Invar alloys, differing from world analogues improved performance characteristics and satisfy the demands high-tech industries in the modern materials for special purposes, as confirmed by an act of implementation (Appendix 11).



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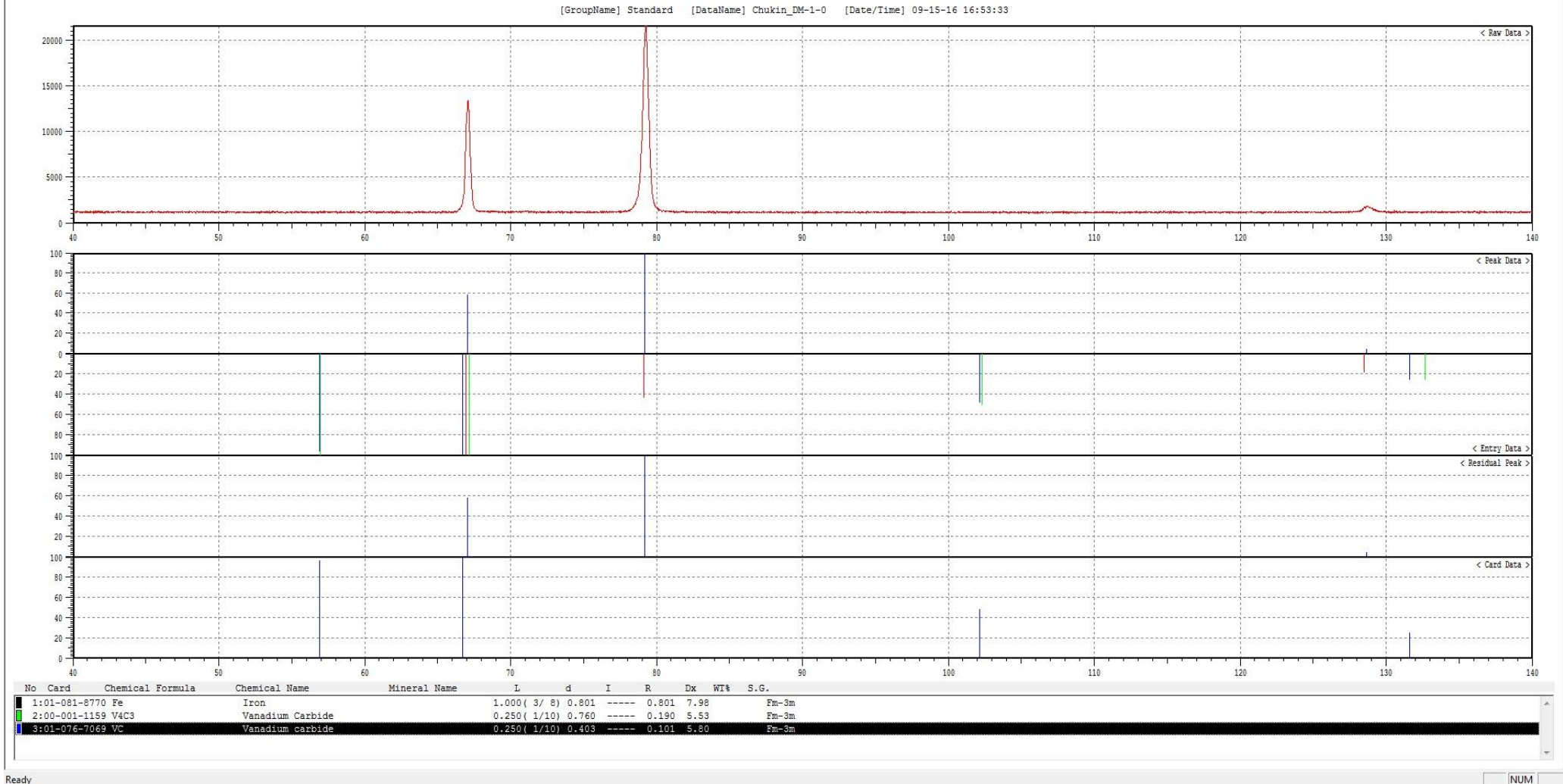
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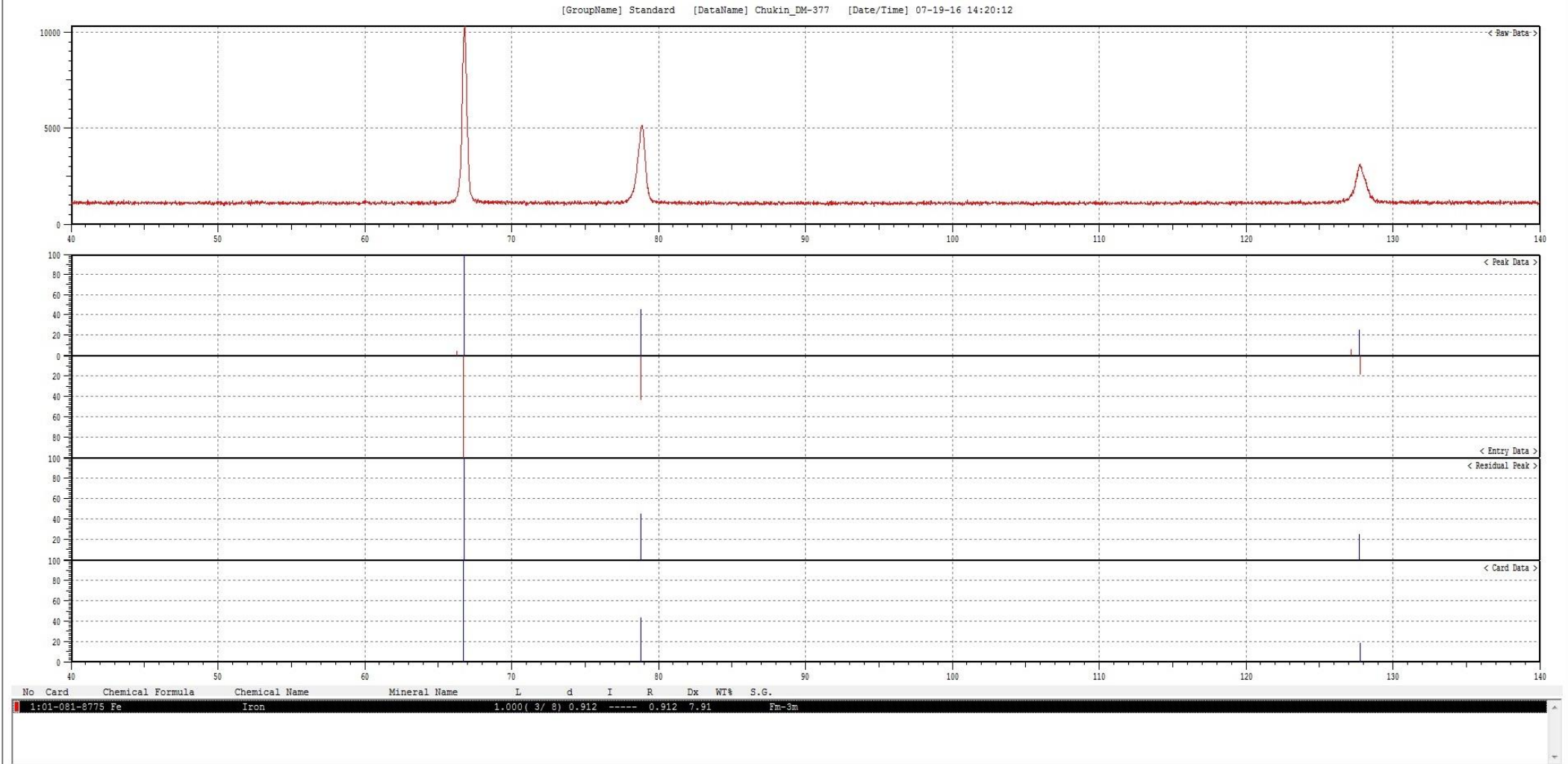
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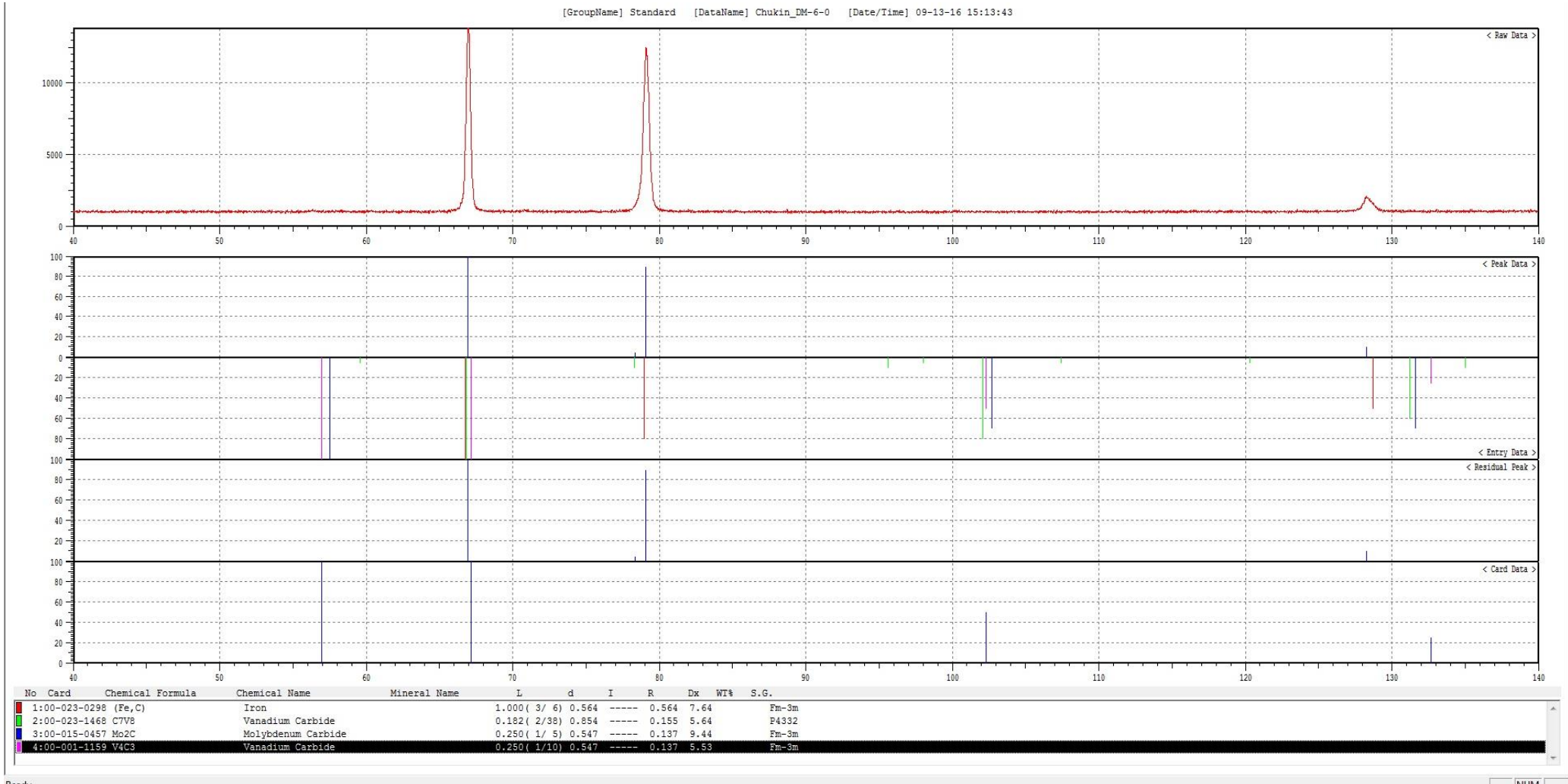
The XRD pattern of the alloy 32NF in the initial hot-rolled condition



The XRD pattern of the alloy 32NFK in the initial hot-rolled condition



The XRD pattern of the alloy 34NFM in the initial hot-rolled condition



Ready

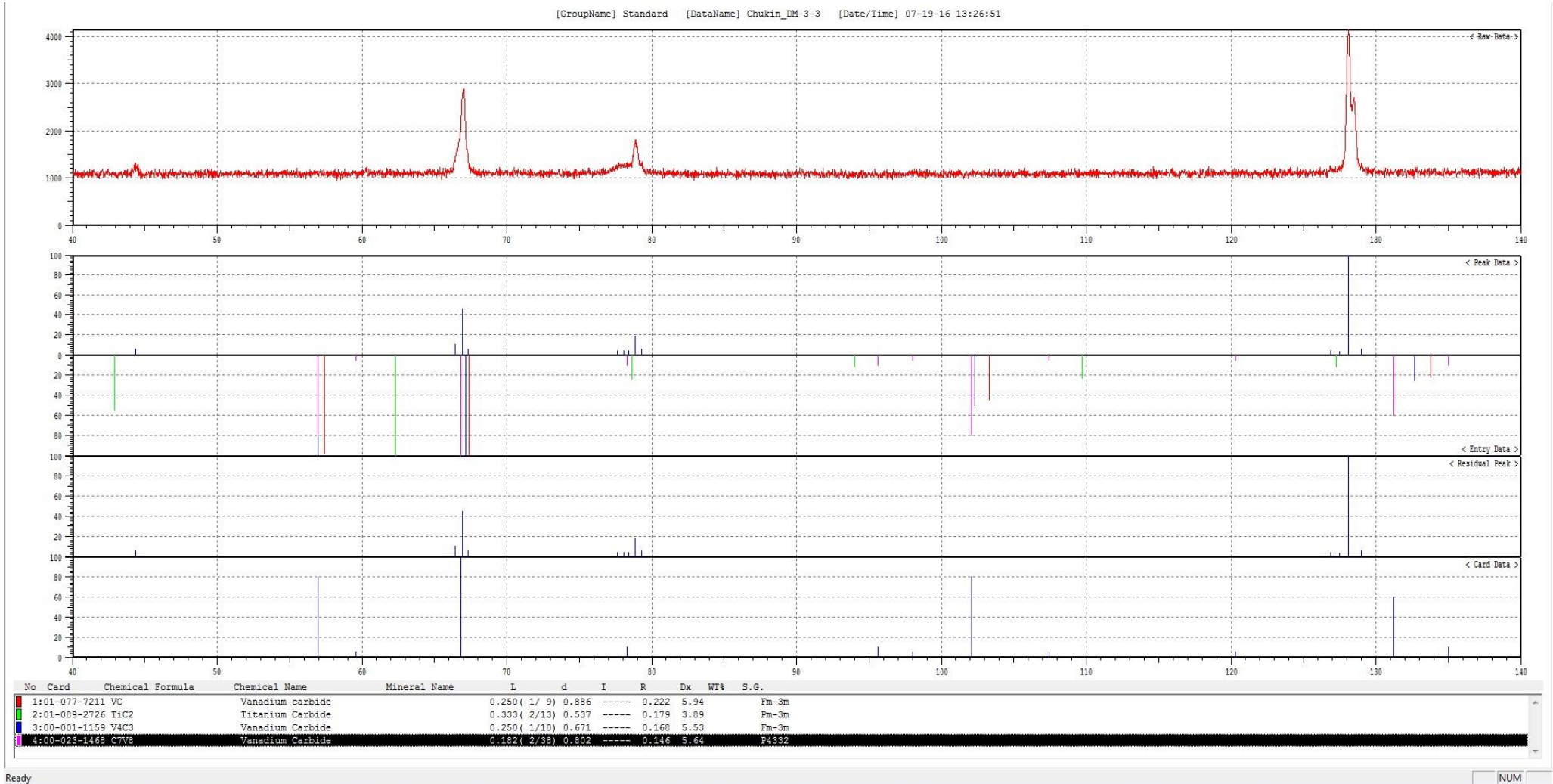
INUM

The crystallographic parameters of the alloys after different heat treatment regimes

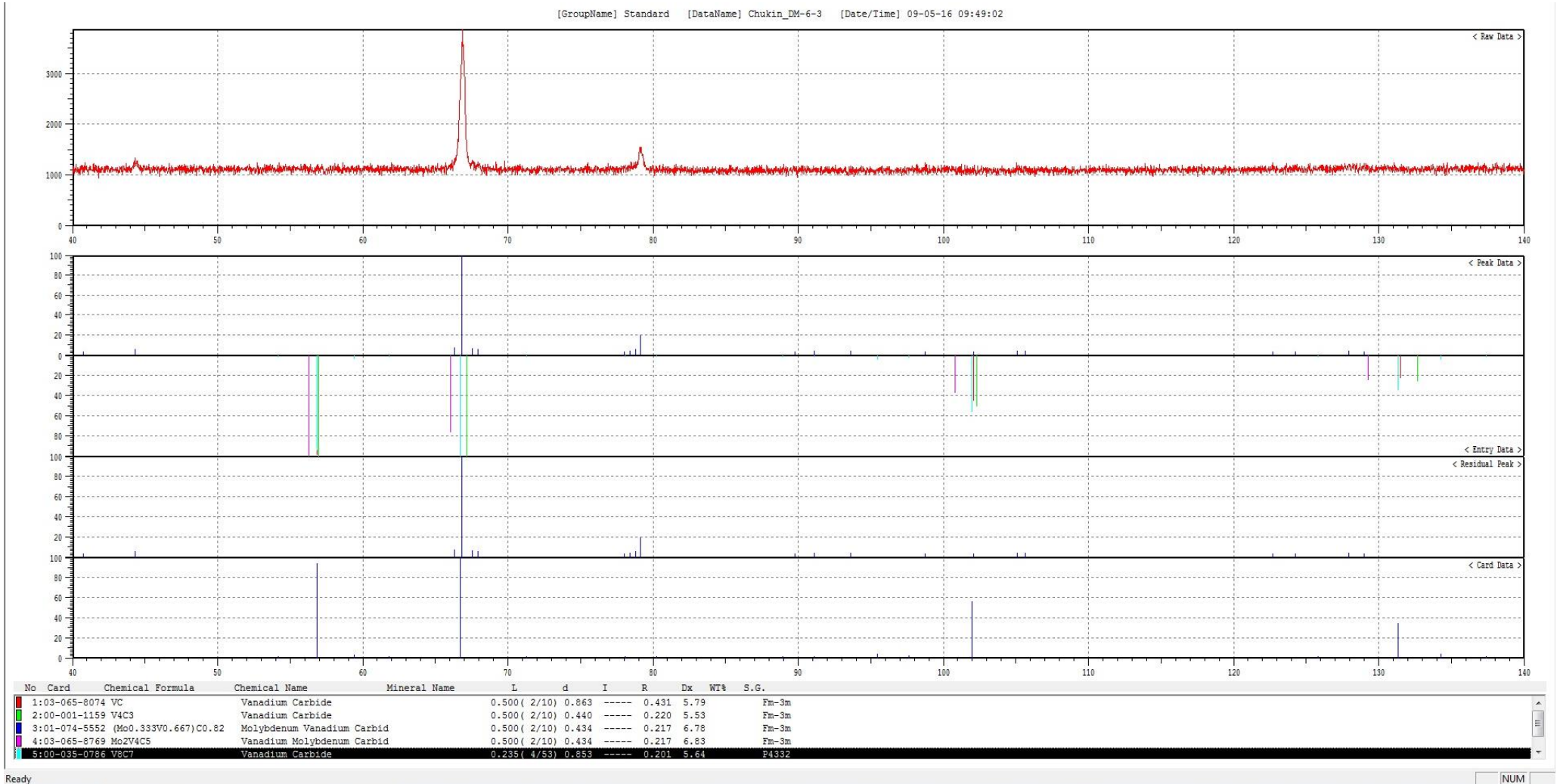
Alloy	Heat treatment	Crystallographic plane	Angle, degree	Interplanar distance, Å	The lattice parameter, Å
32NF	Initial	111	66,77	2,081	3,607
		200	78,80	1,804	
		220	127,70	1,275	
	Hardening from 1250 ° C in water	111	66,96	2,075	3,605
		200	78,87	1,802	
		220	128,11	1,273	
	Aging	111	66,91	2,077	3,624
		200	78,36	1,812	
		220	128,41	1,272	
34NFM	Initial	111	66,94	2,078	3,597
		200	79,08	1,798	
		220	128,26	1,272	
	Hardening from 1250 ° C in water	111	66,85	2,078	3,595
		200	79,13	1,797	
		220	127,95	1,274	
	Aging	111	66,81	2,080	3,598
		200	79,04	1,799	
		220	127,96	1,274	
200		78,70	1,806		
220		127,65	1,276		
32NFK	Initial	111	67,05	2,073	3,591
		200	79,22	1,796	
		220	128,63	1,270	
	Hardening from 1250 ° C in water	111	66,97	2,075	3,596
		200	79,10	1,798	
		220	128,20	1,273	
	Aging	111	66,90	2,077	3,600
		200	79,00	1,800	
		220	128,14	1,273	



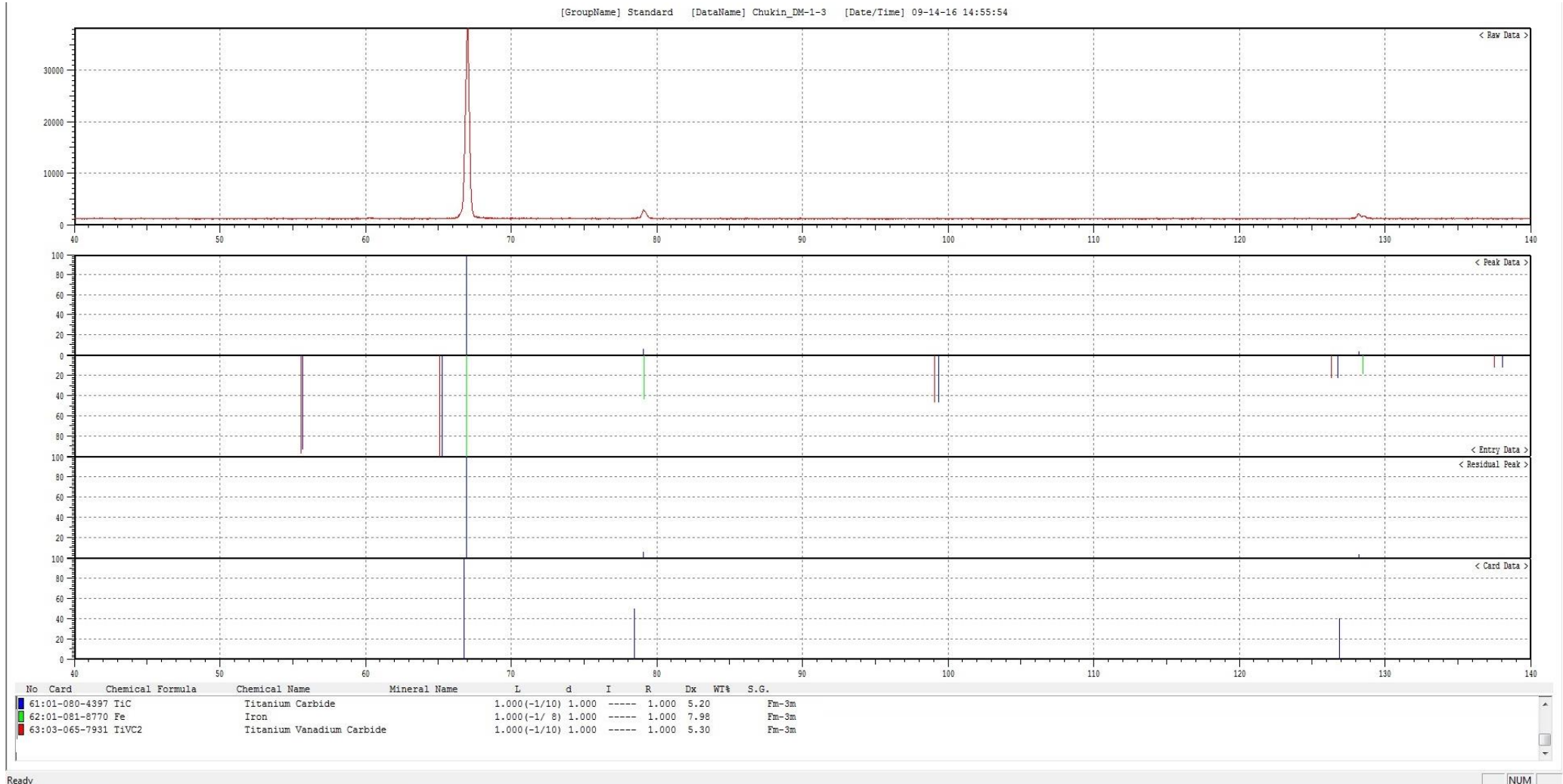
Diffraction pattern 32NF Alloy after quenching from 1250 °C in water



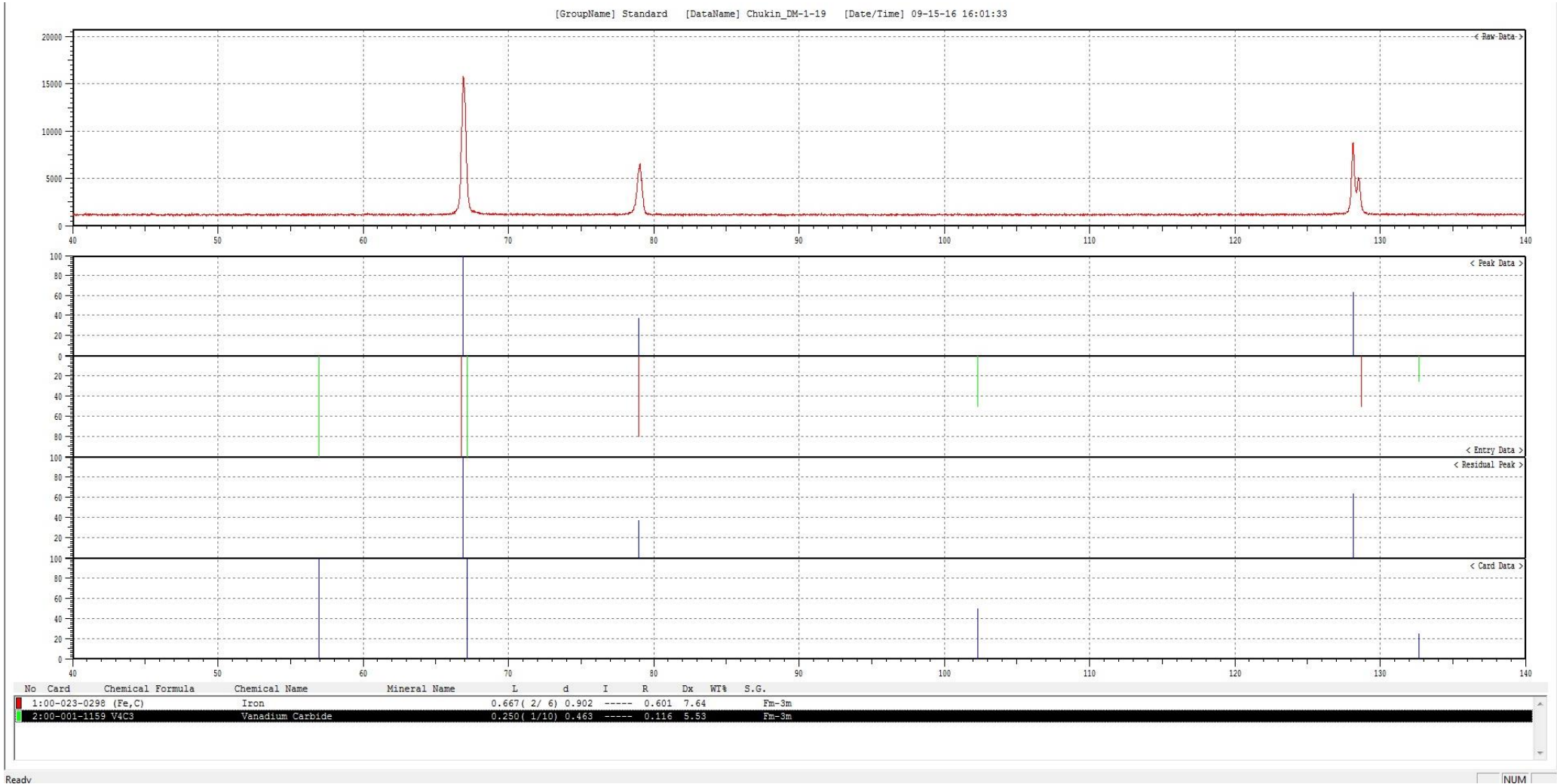
Diffraction pattern 34NFM Alloy after quenching from 1250 °C in water



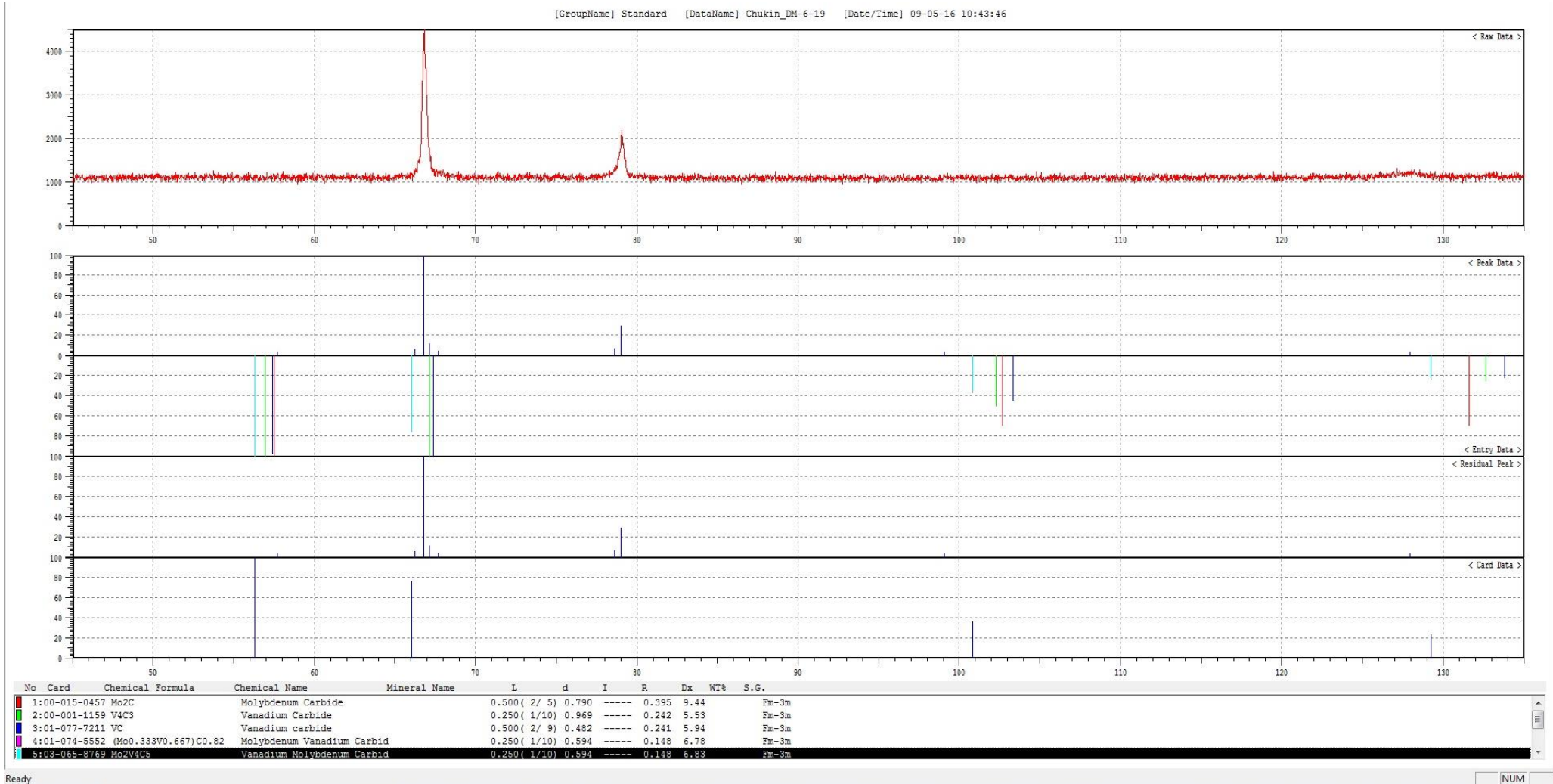
Diffraction pattern 32NFK Alloy after quenching from 1250 ° C in water



Diffraction pattern 32NF alloy after aging at 700 °C quenched from 1250 °C in water



Diffraction pattern 34NFM alloy after aging at 700 °C quenched from 1250 °C in water

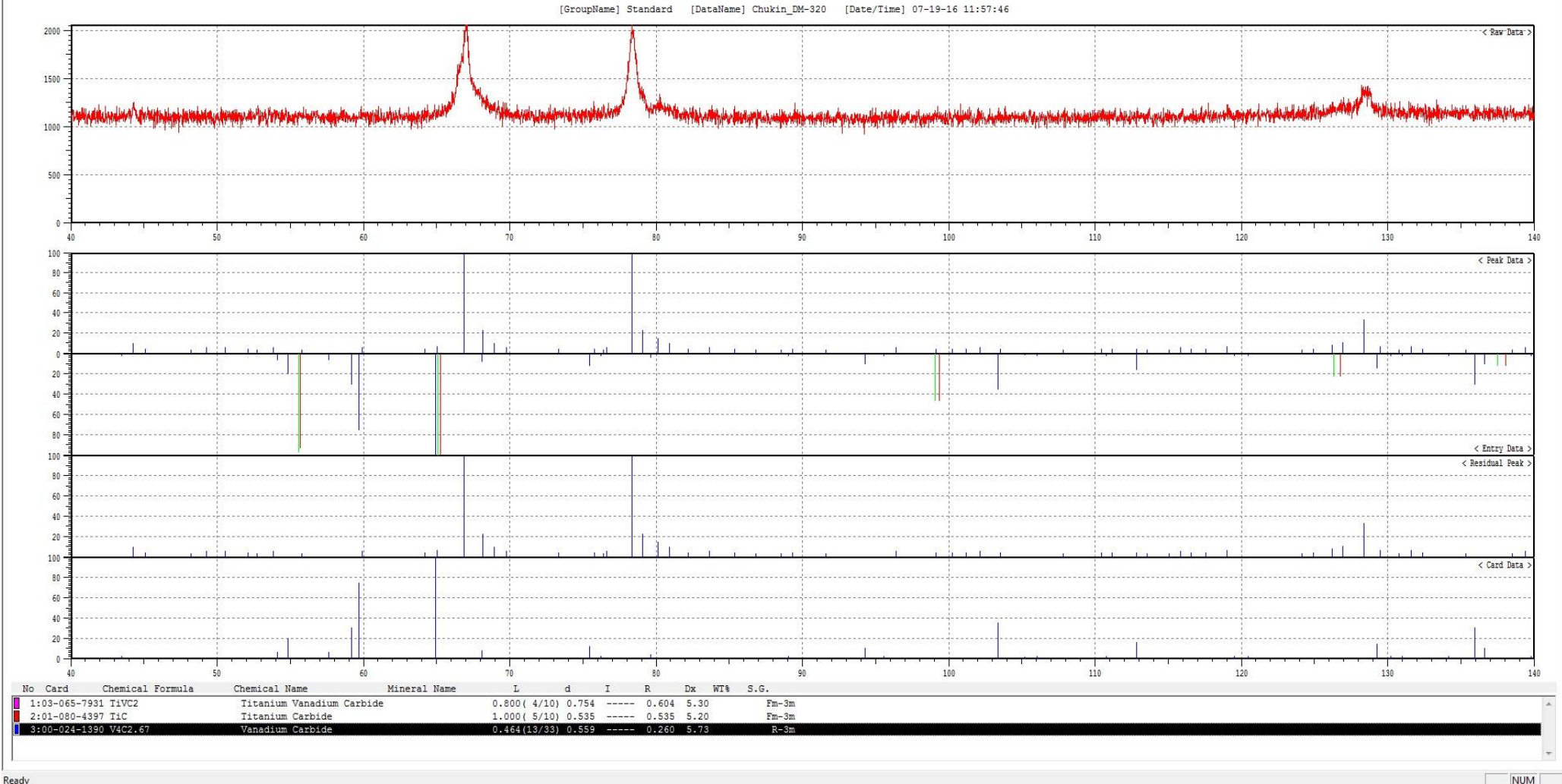


Ready

NUM



Diffraction pattern 32NFK alloy after aging at 650 °C quenched from 1250 °C in water



**УТВЕРЖДАЮ**  
 Заместитель Генерального директора  
 по операционному управлению  
 ПАО «Мотовилихинские заводы»

И.П. Медведев

\_\_\_\_\_ 2016г.

М.П.



### АКТ ВНЕДРЕНИЯ

результатов работ по договору от «20» ноября 2012 г. № 20/11-МЗ  
 с дополнительным соглашением от «11» февраля 2013 г № 1  
 и дополнительным соглашением от «03» июля 2015 г. № 2

с ФГБОУ ВПО «МГТУ»  
 (наименование организации)

**по теме:** Организация малотоннажного производства наноструктурированных заготовок из многофункциональных сплавов со специальными свойствами.

#### Краткое описание выполненной работы

Разработаны химические композиции многофункциональных сплавов, обеспечивающие достижение трудносочетаемых свойств высокого уровня. Разработаны технологические режимы изготовления наноструктурированных заготовок их многофункциональных сплавов со специальными свойствами широкого размерно-марочного сортамента. Проведен комплекс научных исследований структурно-фазовых превращений при термической обработке многофункциональных сплавов, в т.ч., сплавов на основе системы Fe-Ni, легированных углеродом и карбидообразующими элементами. Исследовано влияние режимов термомеханической обработки материалов на уровень физико-механических и эксплуатационных свойств изделий, полученных из данных сплавов. Организовано малотоннажное высокотехнологичное производство заготовок из многофункциональных сплавов со специальными свойствами, отличающихся от мировых аналогов улучшенными эксплуатационными характеристиками и удовлетворяющих потребности наукоемких отраслей промышленности в современных материалах специального назначения.

#### Полученный результат

Разработаны методики исследований физико-механических свойств прецизионных материалов нового поколения в процессах термомеханической обработки.

Проведены исследования, в том числе металлографические, влияния режимов обработки на качество получаемых заготовок.

Проведено обобщение результатов структурного, спектрального анализа наноструктурированных заготовок из многофункциональных сплавов со специальными свойствами, прошедших весь технологический цикл.

Разработаны технологическая инструкция РГ 25000.84509 и маршрутная карта РГ 10000.84508 процесса изготовления наноструктурированных заготовок из многофункциональных сплавов со специальными свойствами.

Предложены рекомендации по регламенту действий технологического персонала ПАО «Мотовилихинские заводы» при освоении нового размерно-марочного сортамента из многофункциональных сплавов.

Разработаны Технические Условия «Прутки горячекатаные и кованные механически обработанные из многофункциональных сплавов со специальными свойствами. Опытная

Continuation of Appendix 11

партия».

Выполнена работа по одобрению, акцептации и сертификации наноструктурированных заготовок из многофункциональных сплавов со специальными свойствами. Получен сертификат соответствия № 1949587, выданный органом по сертификации металлопродукции № РОСС RU.0001.11.ЧС12 от 01.12.2015 г.


Получено 2 патента на изобретения.

Дата фактического внедрения « 01 » 01 2016г.

Срок полезного использования \_\_\_\_\_ 5 \_\_\_\_\_ лет

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Согласовано:  
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ПАО «Мотовилихинские заводы»

Главный металлург  
ПАО «Мотовилихинские  
заводы»

Заместитель Главного технолога по  
инновациям и спецпроцессам  
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ПАО «Мотовилихинские заводы»

	А.Н. Матушкин
	С.Ю. Нижегородов
	Д.П. Подузов



# LIST OF PUBLICATIONS

1. M.V. CHukin, N.V. Kopceva, E.M. Golubchik, D.M. CHukin, E.M. Medvedeva. *The study of heat treatment in the production of a new generation of high-Invar alloys*, Metallurg. - 2014. - № 4. - p. 97-102.
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Efimova, E.M. Medvedeva. Effect of hardening and subsequent aging on the structure and properties of high-strength carbon-containing Invar alloys, alloyed with cobalt, XVI International Scientific Conference “New technologies and achievements in metallurgy, material engineering and production engineering”: a collective monograph / edited by H. Radomiak, J. Boryca / – Czestochowa: Czestochowa University of Technology, Faculty of Production Engineering and Material Technology, 2015. – P. 295-298.

### *Conference*

XIII International Scientific-Technical "Ural Workshop for young scientists - metallurgists" (Ekaterinburg, 2012);

71st, 73rd and 74th International scientific-technical conference "Actual problems of modern science, technology and education" (Magnitogorsk, 2013, 2015, 2016.);

XXII Ural metallurgists school-treater "Actual problems of physical metallurgy of steels and alloys» (Orenburg, 2014);

XIV International scientific and technical conference of young specialists (Magnitogorsk, 2014);

11th International Scientific and Technical Conference "Modern metal materials and technologies (SMMT'15)" (St. Petersburg, 2015);

International symposium "Reliability and Quality" (Penza, 2015);

XIX International Scientific and Practical Conference "Metallurgy: Technology, Innovation, Quality" (Novokuznetsk, 2015);

VI and VII International Congress «Non-Ferrous Metals and Minerals" (Krasnoyarsk, 2014, 2015.);

VI International Conference "Deformation and destruction of materials and nanomaterials" (Moscow, 2015);

International Youth Scientific and Practical Conference "Innovative processes of metal forming: fundamental questions the link between science and production" (Magnitogorsk, 2015);

3rd International Scientific and Practical Conference "Innovative technologies in materials science and engineering (ITMM-2016)" (Perm, 2016).

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